3rd Edition

LEAVING CERTIFICATE

CHEMISTRY LIVE!

DECLAN KENNEDY
RYAN GALLAGHER

FOLENS

3rd Edition

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Cover Design
Wild Apple Design Ltd

Design and Layout
Wild Apple Design Ltd

Illustrations
Adam Wilkinson, Dan Baty, Dog's-ear, Wild Apple Design Ltd.

Index
Kate Murphy

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ISBN 978-1-7892-7247-5

Folens Publishers, Hibernian Industrial Estate, Greenhills Road, Tallaght, Dublin 24.

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Introduction

The third edition of this textbook has been updated to take into account the new Leaving Certificate Chemistry curriculum specification introduced into schools in September 2025. All the material for Higher and Ordinary level students is included in this textbook. All Higher Level material is indicated by a vertical line drawn down the left-hand side of the margin.

All topics are covered to the depth indicated in the published curriculum specification. We hope that the numerous Worked Examples will help students to gain an understanding of the key topics on the course as well as an appreciation of the type of answer required in Leaving Certificate examination papers. We are very fortunate to have copies of SEC Sample Examination Papers to inform us of the style and format of examination questions that will be used when designing future examination papers. The numerous Worked Examples are available not only in the textbook but are also available online. These online Worked Examples are signposted throughout the textbook.

As in *Chemistry Live* 2nd Edition, some topics (chapters 23–26) are included in the accompanying *Assessment and Exam Guide*. The inclusion of these chapters in the *Assessment and Exam Guide* has enabled us to ensure that the correct depth of treatment has been applied to all chapters in both the textbook and in the *Assessment and Exam Guide*.

All the Student Experiments listed on the syllabus are included in this textbook. The key points of each experiment are included in the textbook and full step-by-step instructions are given in the accompanying *Student Laboratory Notebook*. A full list of Student Experiments in the order in which they appear in the textbook is given on the following pages.

In keeping with the learning outcomes in the Unifying Strand, throughout the textbook and online materials we have emphasised the importance of Science, Technology and Society (STS) and included references to the contributions that famous scientists have made to scientific discoveries and their impact on society. We also give students an appreciation of how scientists work and how scientific ideas are modified over time as required by the curriculum specification.

We have not assumed any previous knowledge of chemistry among the students for whom this textbook is written. For this reason, the opening chapters of the book introduce students to the fundamental concepts of chemistry before moving on to some of the major areas of the curriculum.

The use of the letters [LCH] and [LCO] after a question indicates that this question is taken either from a past Leaving Certificate Higher or Ordinary level paper, respectively. It is strongly recommended that students use the *Assessment and Exam Guide* in conjunction with the textbook. Questions in the *Assessment and Exam Guide* are prefixed by the letter W. These questions play an important role in testing the student and in preparing him/her for the Leaving Certificate examination. The permission of the State Examinations Commission to reproduce questions from past Leaving Certificate examination papers is gratefully acknowledged.

Writing this textbook has been a very challenging and enjoyable task and we are extremely grateful to our many friends and colleagues who have given us so much support and encouragement. In particular, we wish to express our sincere thanks and deep gratitude to those who proof-read some or all of the manuscript and made very useful suggestions and comments on the material. The comments of the proof-readers have helped us greatly in the production of the final draft of this textbook. We also wish to thank Lennox Laboratory Supplies and PASCO Scientific for their assistance in providing equipment for use in the online videos and photographs included in this publication.

A special word of thanks to our families for their help and support in writing this textbook.

Last but not least we wish to express our sincere thanks and appreciation to the staff at Folens with whom it has been a pleasure to work: Conor Walker, Ciarán Deane, Michael Plunkett and Clodagh Quinn; as well as Emma Farrell and Rónán Vaughan at Dog's-ear. Their hard work and dedication has ensured that the *Chemistry Live* teaching package is of the highest possible standard.

We wish all students who use this textbook and the accompanying resources every success with their studies. Bail ó Dhia ar an obair!

Declan Kennedy, Ryan Gallagher

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The Experiment numbers refer to the Student Experiment numbers as given in *Chemistry Live!*

Laboratory Practical Work

Chemistry is a subject that involves a lot of practical work. The experiments in this book will help you to develop many practical skills and to gain confidence in working in the laboratory. Practical work also provides an opportunity for you to work with your classmates as part of a team. Above all, practical work will help to maintain your interest in chemistry, enhance your understanding of the subject and make chemistry more enjoyable for you.

Laboratory Safety

When carrying out experiments in the laboratory, safety is of the utmost importance. Even though most accidents that occur in school laboratories are of a minor nature, there is the potential in school laboratories for serious accidents to occur. To avoid accidents, it is important that you follow the laboratory rules and that you understand the safety symbols associated with the chemicals that you use in the laboratory.

Laboratory Rules

Most laboratory rules are based on normal common sense and are designed to ensure that the laboratory is a safe and healthy environment in which to work. The following set of suggested laboratory rules should be studied carefully. Your teacher may wish to modify these rules to make them more appropriate to the circumstances of your own school.

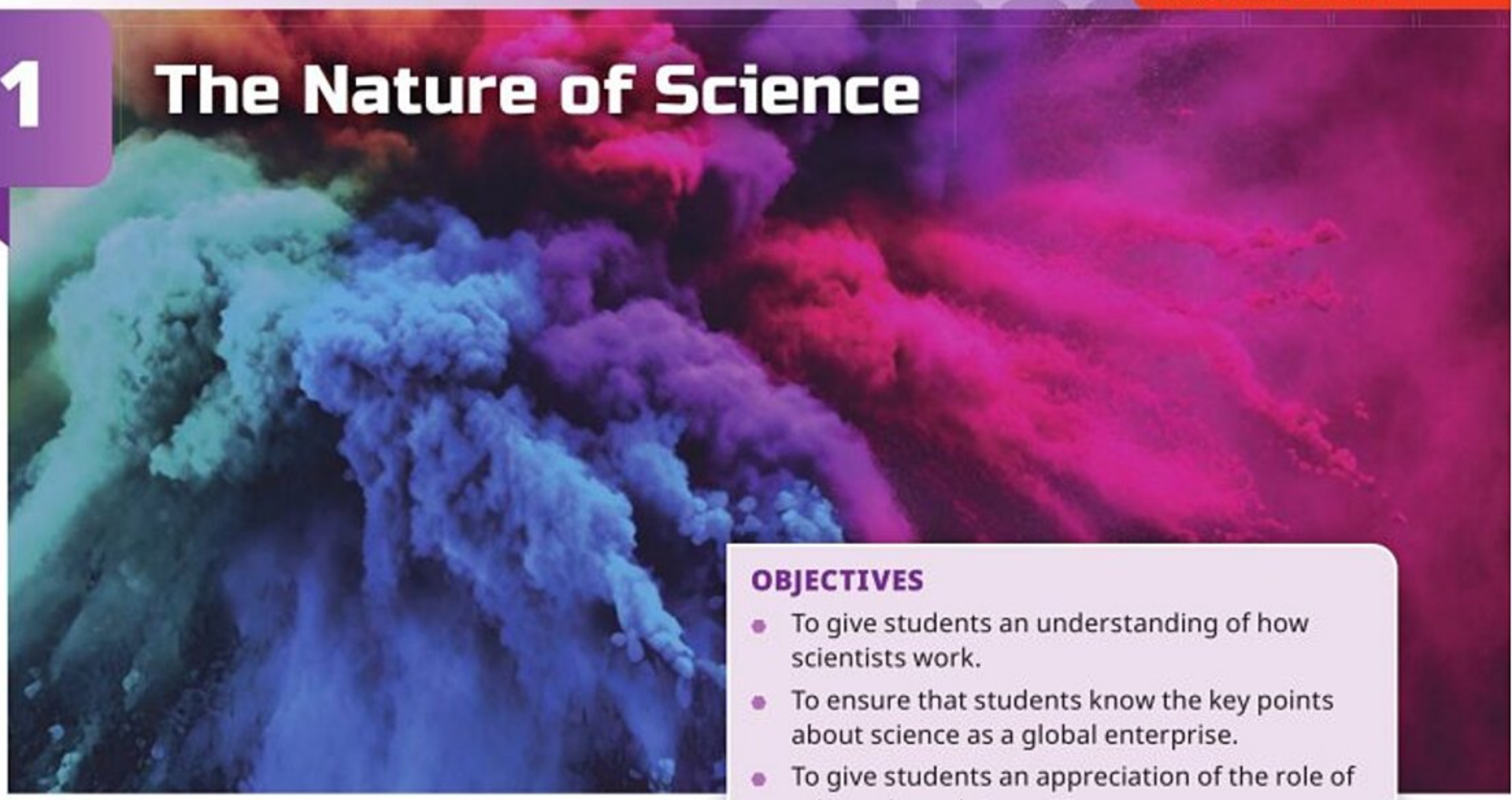
1. Follow all directions exactly as given by your teacher.
2. Perform only those experiments assigned to you by your teacher.
3. Safety glasses should be worn during all practical classes unless your teacher indicates otherwise.
4. When heating a liquid in a test-tube, place the test-tube in a beaker of warm water rather than heating it over a Bunsen burner.
5. If heating a test-tube, never look into the mouth of the test-tube. Never point the mouth of the test-tube in the direction of any other person during the heating process.
6. Never use a naked flame to heat a flammable liquid, e.g. alcohol.
7. Never force glass tubing into or out of rubber stoppers or tubing. Use a small amount of glycerine or Vaseline as a lubricant. Always ensure that your hand is protected by a thick cloth or suitably thick gloves.
8. Regard all laboratory chemicals as poisonous. Chemicals should never be tasted. If you get something into your mouth, spit it out immediately, wash out your mouth with water and report the accident to your teacher.
9. Test for odours of gases by wafting your hand over the sample and sniffing cautiously.
10. Take care when handling corrosive liquids (e.g. concentrated acids) and only use these liquids under the direct supervision of your teacher.
11. Never rush around the laboratory. This can be very dangerous.
12. Do not bring coats into the laboratory. Put your bag in a place where it will not cause somebody to fall over it.
13. Always co-operate with your teacher and fellow students. As well as learning about chemistry, it is important that you learn to work as part of a team.
14. Any accident or injury, however slight, must be reported to your teacher.
15. Before you leave the laboratory, wash any glassware you have used, make sure that all the apparatus has been put back in its correct place and leave the bench clean and dry.

Safety Symbols

As you use various chemicals in this course, you will observe safety symbols on the containers in which these chemicals are stored. The relevant safety symbols are also printed next to the experiments described in this book and in the Chemistry Live Student Laboratory Notebook. These symbols will remind you of the safety precautions you must adopt when using these substances. You must learn to recognise these symbols and understand their meaning. The main safety symbols are shown below.

Safety Glasses	Harmful or Irritant	Flammable	Corrosive	Toxic	Oxidising	Explosive
Eye protection must be worn.	These substances are less of a health risk than toxic substances. However, they must still be handled with care.	These substances may easily catch fire in a laboratory under normal conditions.	These substances can cause chemical burns to skin and eyes.	These substances may cause serious health risks or death if inhaled, swallowed or if they penetrate the skin.	These substances may produce much heat when they react with other substances, particularly flammable substances.	These substances may explode if ignited in air or exposed to heat. A sudden shock or friction may also cause an explosion.

1 The Nature of Science



OBJECTIVES

- To give students an understanding of how scientists work.
- To ensure that students know the key points about science as a global enterprise.
- To give students an appreciation of the role of science in society.

1.1 Introduction

The word 'science' comes from the Latin word *scientia* which means 'knowledge'. Science is the study of the natural world around us. Scientists try to provide accurate explanations of how the natural world works.

The branches of science that study the natural world around us are referred to as the **natural sciences**. On the other hand, the branches that study human behaviour and society are called the **social sciences**. The natural sciences are divided into **physical science** and **biological science**. Physical science is that branch of science that deals with inanimate (non-living) things. It is subdivided into subjects such as physics, chemistry, astronomy, geology and computer science. Biological science is that branch of science which deals with living things. It is subdivided into botany (the study of plants), zoology (the study of animals) and microbiology (the study of micro-organisms).

In this course, we will be studying the subject of chemistry in some detail. Chemistry describes the substances found in nature. It investigates what these substances are made of, how they react with one another, and how new substances are produced. Without the ability of chemists to make new substances, we would have no medicines to keep us healthy, no colourful clothes to wear, no soap to keep us clean – and no deodorant or perfume or aftershave to help us smell nice!

1.2 How scientists work

Similar to all scientists, chemists are curious people – they want to understand how the world works. To do this, they follow a logical and organised process called the **scientific method**, Figure 1.1. This is a step-by-step approach that helps us test ideas, answer questions and discover new knowledge.

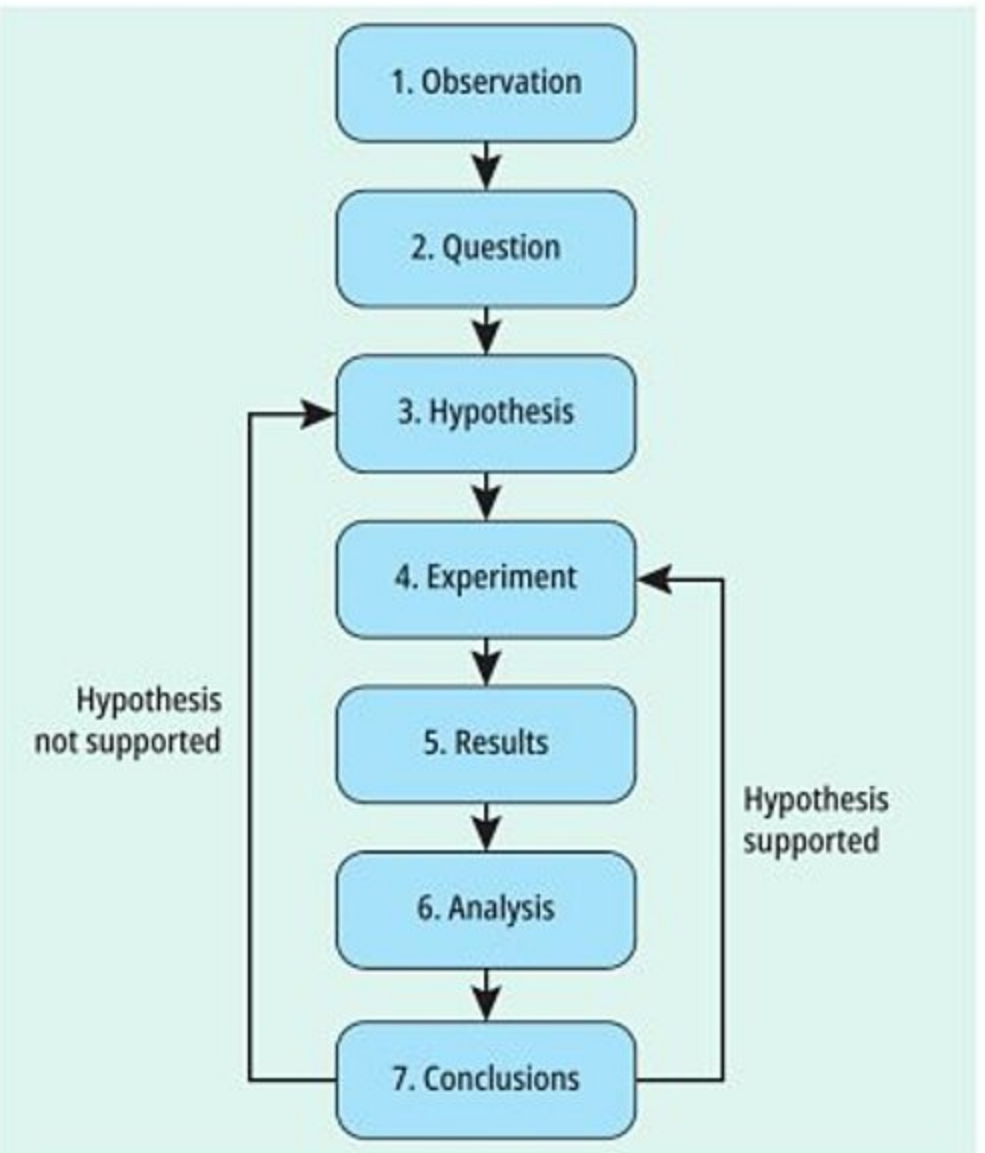


Figure 1.1 Summary of steps involved in the scientific method

- The scientific method starts with an **observation**. This involves noticing something interesting in the chemical world. For example, a student may observe that marble chips may react more slowly with a dilute acid than with a concentrated acid.
- Arising out of this observation is the **question**. For example, the question might be: *What is the relationship between the concentration of the acid and the rate of the reaction?*
- The next step is to propose a **hypothesis**.

A hypothesis is a proposed explanation of why certain events take place.

A hypothesis is an 'educated guess' or a proposition or a suggestion to explain what is happening when we are carrying out a scientific investigation.

A hypothesis is like a suggested explanation that has not yet been proven. A hypothesis is always written in the form of an 'if ... then' statement. For example, the hypothesis for the reaction between the marble chips and acid could be: 'If I increase the concentration of the acid, then the rate of the reaction will increase.' Note that this prediction is very clear.

- The next step is to carry out an **experiment** to test the hypothesis. The student might decide to react equal masses of marble chips of similar size with HCl of different concentrations and measure the mass of CO_2 produced over a certain period of time. In the Leaving Certificate chemistry course, we will be carrying out a wide variety of laboratory practical work. In these experiments we will be collecting data. In some cases, the data we collect will be numerical data, i.e. we will measure quantities such as mass, volume and time. This type of data is called **quantitative data**.

Quantitative data are numerical measurements that are made using scientific instruments. Examples of quantitative data are values of mass, temperature, volume and time.

In other experiments, we will test for the presence of certain substances in materials. For example, we will be identifying the presence of some metals in salts or testing for the presence of specific ions in solution. In these cases, we will be making observations, e.g. colour changes taking place, a solution becoming cloudy, gases being given off or a description of the flame when a gas is burned. These types of data are called **qualitative data**.

Qualitative data are descriptive observations that are made by the person carrying out the experiment. Examples of qualitative data are changes in colour or observation of a gas being produced.

- The **results** of the experiment are collected and the data are summarised in the form of tables and graphs. The experiment is repeated a number of times to ensure that the results are reliable. A measurement is reliable if we repeat the same experiment and we get the same or similar results over and over again.
- The data **analysis** part of the scientific method then takes place. This is one of the most important parts of the experiment. Without collecting reliable data and analysing it carefully, we cannot draw valid conclusions.
- Having analysed the data, we then draw **conclusions**. These conclusions will help us to decide if the data supports or does not support the hypothesis. If the conclusions support the hypothesis, then the experiment is repeated a number of times to help to validate the results. A conclusion from the above experiment might be that the rate of reaction is directly proportional to the concentration of the acid. If the conclusions do not support the hypothesis, then a new or modified hypothesis will have to be developed.

Note on Research Investigation: It is proposed as part of your studies in this chemistry course that you will carry out your own research investigation. Carrying out the laboratory practical work that is specified on the curriculum will be of huge help to you in acquiring the laboratory practical skills necessary to carry out the research investigation. Online resources, including details of how to carry out research investigations, types of variables and carrying out risk assessments will be available in the online resources accompanying this textbook. These online resources will help to guide you in carrying out your research investigation. These online resources will be regularly updated in the light of information received from the State Examinations Commission and exam marking schemes. Therefore, details of how to carry out research investigations will not be discussed further in this chapter.

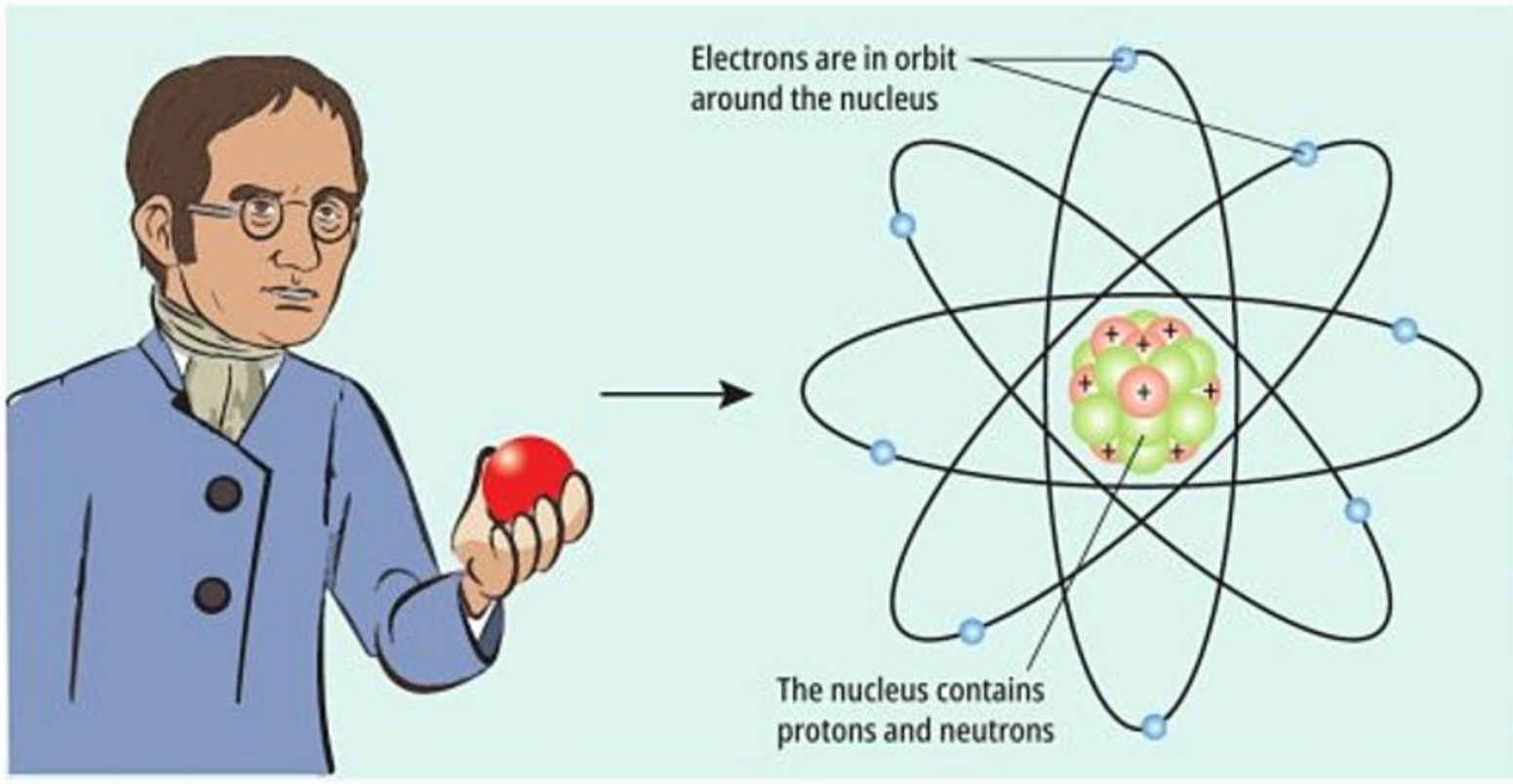


Figure 1.2 John Dalton's simple model of the atom had to be changed when it was discovered that sub-atomic particles existed.

1.3 How scientific ideas are modified over time

You may recall coming across the word 'theory' in your study of science at Junior Cycle level, e.g. the particle theory that was used to explain the properties of solids, liquids and gases. Scientific theories are based on lots of observations and experimental results and, in general, are accepted by scientists around the world.

A **scientific theory** is an *explanation* of observations and is based on hypotheses, laws and facts.

In this course, we will be studying theories such as atomic theory and acid–base theories. It is important to realise that scientific ideas change as new evidence is discovered and improved technology is developed to help chemists collect better quality data. For example, in Chapter 2 we will learn about the atomic theory put forward by John Dalton in 1808. The model of the atom proposed by Dalton was that atoms were like snooker balls that cannot be broken down into simple particles, Figure 1.2. However, this model had to be changed to a more modern model when it was discovered that smaller particles (called sub-atomic particles) existed inside the atom.

In other words, our understanding of chemistry ideas improves as new discoveries are made and new models are developed.

You may also recall meeting the idea of scientific laws in your study of science at Junior Cycle level. For example, you studied the Law of Conservation of Mass and learned that when a chemical reaction occurs, the total mass of the reactants is always equal to the total mass of the products. Antoine Lavoisier based this law on repeated observations and experiments. He did not understand why the law was true – he just stated his observations.

A **scientific law** is a *description* of observed occurrences.

In short, a scientific theory **explains** why something happens but a scientific law **describes** what happens. Theories can change if new evidence is found. However, laws rarely change.

1.4 Science as a global enterprise

The phrase 'science as a global enterprise' means that the work carried out by scientists is not just something that happens in one country or in one laboratory. On the contrary, it is a worldwide team effort where scientists all around the world work together, share their knowledge and skills, and follow the same rules and standards. This allows them to achieve beneficial and reliable results to help solve problems facing people all over the world, Figure 1.3.

Figure 1.3 Scientists all over the world study similar problems such as combating diseases, climate change and developing new biodegradable plastics.

- **Science relies on evidence.** Scientific ideas must always be based on evidence, i.e. data gathered by means of careful observations and scientific investigations. For example, Niels Bohr put forward the idea of electrons in orbit around the nucleus as a result of evidence gathered from studying the light given out when certain elements were heated.
- **Clear communication.** Scientists must be able to explain their ideas and discoveries clearly so that other scientists around the world can understand and make use of these ideas and discoveries. For example, chemists throughout the world use the same symbols for the elements in the Periodic Table and the same methods of writing balanced chemical equations.
- **International conventions.** Scientists around the world adopt the same regulations (conventions) and systems when writing up reports of their work. For example, IUPAC (International Union of Pure and Applied Chemistry) is the organisation that sets the rules for naming elements and compounds. Similarly, chemists agree to use the SI (Système International d'Unités) system for units such as length, mass and time. This makes it easy to compare measurements made in one country with those made in other countries.
- **Peer review.** When scientists carry out research, their findings are usually published in scientific journals or books. However, before the research reports are published, the work is reviewed by other scientists who work in that field, Figure 1.4. These scientists are called peers, since they work in similar areas to the authors of the research articles. The editor of the journal or book will send the research article to other scientists who have expertise in the specific area. These other scientists will check if the research work has been carried out correctly and if the conclusions are valid. This ensures that articles with mistakes or false claims are not published.
- **Repeatability.** If a scientist carries out an experiment and obtains a particular result, then if the method is reliable, the same results should be obtained by the same person when repeated using the same method. This process is called **repeatability**. In other words, repeatability means that an experiment can be done again by the same person using the same method and getting the same results. Repeatability ensures that the results are not just a one-time 'fluke'. If repeatability does not exist, then the results cannot be considered reliable.
- **Reproducibility.** If a scientist publishes a method for carrying out a particular experiment in the laboratory, reproducibility is a measure of how different people in different laboratories can get the same results by following the same procedure. Note the distinction between repeatability and reproducibility. Repeatability refers to the same person, carrying out their own experiment, following the same method and getting the same results. Reproducibility refers to different people following the same method in a different laboratory and getting the same results. In chemistry, reproducibility of results is particularly important in the development of new drugs. These drugs are only approved after many scientists in labs around the world obtain the same results under the same conditions.

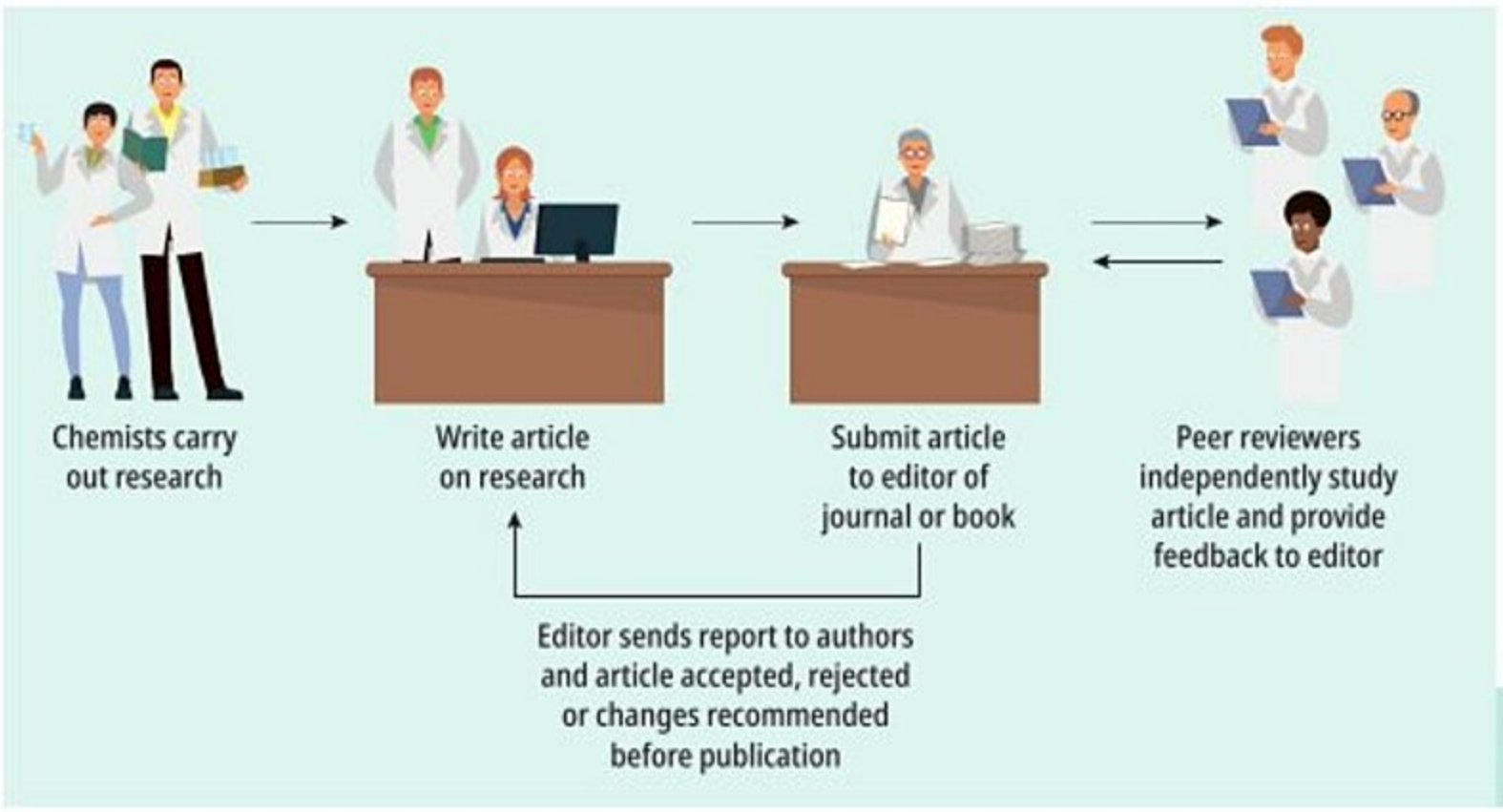

Chemists carry out research
Write article on research
Submit article to editor of journal or book
Peer reviewers independently study article and provide feedback to editor
Editor sends report to authors and article accepted, rejected or changes recommended before publication

Figure 1.4 The peer review process

1.5 Models in chemistry

Chemistry explains how and why substances change, e.g. why adding an indigestion tablet to water causes fizzing, why iron rusts, or why light and heat are given out when a firework explodes. In chemistry we have to explain what we see on a large scale (macroscopic scale) by referring to things that we cannot see, e.g. atoms, molecules, ions and electrons (microscopic scale). Therefore, we use models to help us visualise many of the concepts that we meet in chemistry. In short, models help us to translate what we observe into what is happening in terms of atoms, molecules and other similar species. (In this context, the word 'species' refers to chemical units such as atoms and molecules – it has no connection to the biological term.)

A **scientific model** is a simplified representation to help us to visualise, explain and understand chemistry concepts as well as making predictions about results of physical and chemical changes.

Interpreting models helps us to improve our visualisation skills and logical reasoning skills. Models can be in the form of diagrams, animations, three-dimensional models and computer simulations. You have already met models in your study of Junior Cycle chemistry. For example, when discussing the particle theory, you may recall that the model shown in Figure 1.5 was used to help you understand what happens when a liquid boils. This diagram helps you to link what you observe when a liquid boils, to the theory that explains the process of boiling.

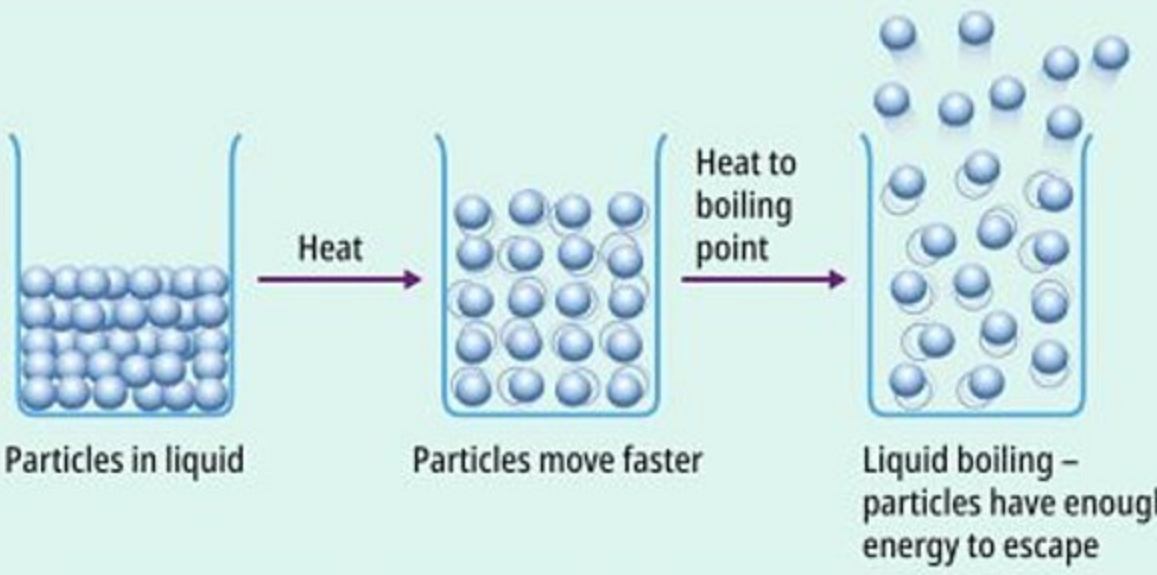

Heat
Heat to boiling point
Particles in liquid
Particles move faster
Liquid boiling – particles have enough energy to escape

Figure 1.5 This model helps us to understand that at the boiling point of a liquid, the water molecules break away from all parts of the liquid and form a gas.

The main points about models in chemistry may be summarised as follows:

- Models may be compared to a **bridge** that helps us to go from the visible (macroscopic) to the invisible (microscopic). They help us to get a picture in our minds of what is happening at the microscopic level. Models help us to be good visual thinkers. Models help us to gain understanding and build pictures in our minds to help us understand many concepts in chemistry that we will meet in this textbook. In particular, we will make a lot of use of models in diagrams to help you to link observations with theory. Also, you will be using three-dimensional *Molymod* kits to help you understand shapes of molecules and chemical bonding. In addition, there are lots of simulations and animations online to help you visualise chemical processes in action.
- Models are **simplified representations** of complex systems. For example, in three-dimensional *Molymod* models, we represent a chemical bond by means of a length of plastic joining two atoms. This model works perfectly to help us understand chemical bonding. However, it is a simplified representation in terms of how a chemical bond is actually formed. Therefore, although models make complex ideas easier to understand, it is important to realise that **models have limitations**.

- **Models can be modified over time.** Models can evolve as more scientific knowledge becomes available. We have already seen that Dalton's simple model of the atom had to be changed when sub-atomic particles were discovered. Models may be compared to tools that help us to understand ideas in chemistry, taking into account all the information available at the present time.
- **Models are very useful for making predictions.** An example of this type of prediction is the use of the particle model to predict that if we decrease the volume of a gas in a container, we will increase the pressure, Figure 1.6.

At present, scientists are using mathematical models and computer simulation models to understand how the climate system of the Earth works. These models are helping to predict details of what might happen in the future in particular areas of the world as a result of global warming.

Even though we cannot see species such as atoms, molecules and ions, models help us to make sense of them. This is why chemistry is such a fantastic subject – it helps you to become a sharper and more scientific thinker. In short, the study of chemistry is good for your brain!

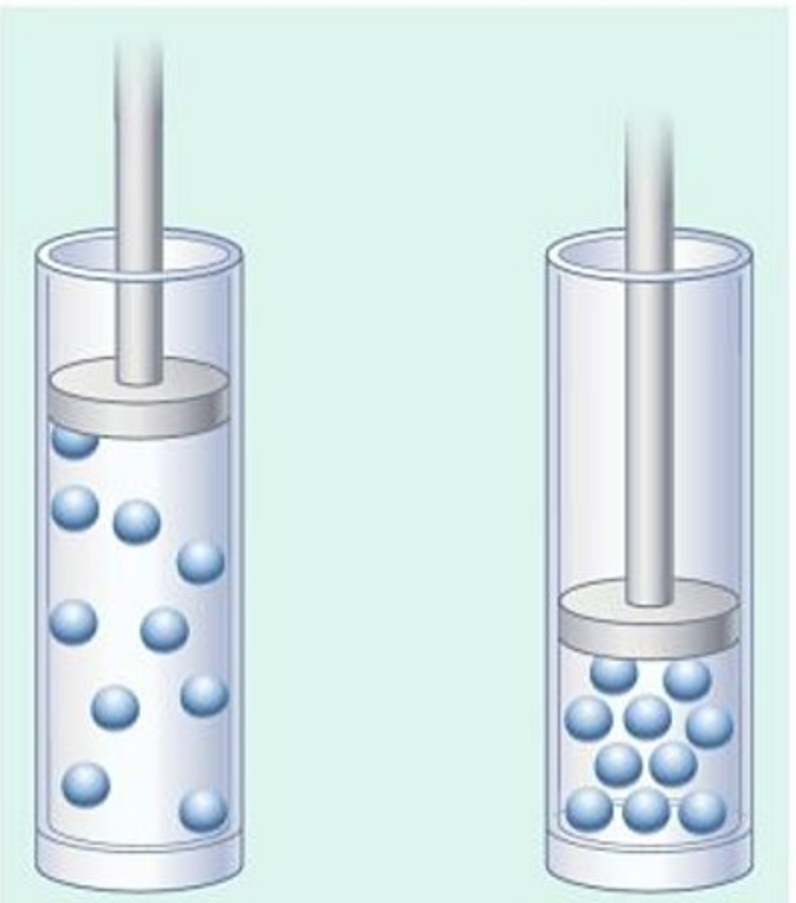


Figure 1.6 The model of the particle theory predicts that if we decrease the volume of the container, the pressure of the gas will increase as more molecules are pushed into a smaller space.

1.6 Chemistry in society

Chemistry is not just a subject that you study in school. Chemistry plays an important role throughout our daily lives and in society.

- **Chemistry and health.** Chemistry plays an important role in the development of medicines, e.g. vaccines, antibiotics and drugs for pain relief. In addition, important drugs have been developed in the area of chemotherapy for cancer treatment as well as anaesthetics for administering to patients undergoing surgery. Chemists play a key role in designing and synthesising drugs. Millions of lives have been saved by vaccines developed by chemists, Figure 1.7. The discovery of penicillin by Alexander Fleming has revolutionised infection control in medicine. Antibiotics are now manufactured in laboratories all over the world. Without these antibiotics, simple infections could be very harmful to our health.
- **Chemistry and technology.** Chemists are involved in the development of lithium-ion batteries for use in items such as smartphones and laptops. In addition, chemists develop solar panels, touchscreens, silicon chips and other items that are essential for the electronics industries. Also, chemists who specialise in the area of materials chemistry are involved in developing modern materials such as touchscreens and polymers used in 3-D printing.
- **Chemistry and sustainability.** A lot of research is taking place in the area of developing biodegradable plastics, carbon-capture processes to remove carbon dioxide from industrial emissions, new catalysts to improve efficiency in the area of industrial chemistry and the development of biofuels from plants.

Figure 1.7 This photograph shows a team of chemists working as part of a drug design team to develop new drugs to treat cancer patients.

It is worth noting that society plays an important role in influencing research in chemistry. For example the search for vaccines during the COVID-19 pandemic drove research into developing an mRNA COVID vaccine. Similarly, the awareness of problems related to climate change is driving research into green energy solutions such as hydrogen fuel cells (Chapter 22).

Each of us has the responsibility to be more personally effective in addressing the impact of science and technology on society. For example, we should make more responsible personal choices such as choosing products with less packaging, using biodegradable materials where possible, and by reducing personal energy consumption with the aid of energy-efficient devices. We should also stay informed by following reliable sources of scientific information and ensure that we understand scientific issues.

In conclusion, it is clear that chemistry plays a key role in every part of our daily lives. It helps protect our health through the development of medicines. It also plays an important role in the development of modern materials used in electronic devices. It is at the heart of global research to help build a more sustainable future through the development of biodegradable plastics, cleaner energy sources and more efficient industrial processes.

It is no wonder that chemistry is often called the creative science. You are about to begin your journey of studying chemistry and we look forward to accompanying you on this journey through *Chemistry Live*!

TEST YOURSELF: Attempt Questions 1.1–1.4 and W1.1–W1.4.

Summary What I should know

- The **scientific method** is a step-by-step approach that helps us test ideas, answer questions and discover new knowledge.
- A **scientific theory** is an explanation of observations and is based on hypotheses, laws and facts.
- A scientific law is a description of observed occurrences.
- A scientific model is a simplified representation to help us to visualise, explain and understand chemistry concepts as well as making predictions about results of physical and chemical changes.
- Chemistry plays an important role in our lives, especially in the areas of health, technology and sustainability.

Learning outcomes

At the end of this chapter, I should be able to:			
Describe how scientists work as they implement the scientific method.			
Explain what is meant by science as a global enterprise.			
Discuss the role of models in chemistry.			
Outline the important role that chemistry plays in society.			

Chapter review questions

1.1 **(a)** Explain what is meant by the term *natural sciences* and give two examples.

(b) Distinguish between natural sciences and social sciences.

(c) What is the difference between physical science and biological science?

(d) What is meant by the term *scientific method*?

(e) What is the first step in the scientific method and what does it involve?

(f) Define the term *hypothesis* in the context of scientific investigations.

(g) Write a hypothesis for the question: *What effect does temperature have on the rate of a reaction?*

(h) Distinguish between quantitative and qualitative data and give one example of each.

(i) What are two typical observations that would be recorded as qualitative data during an experiment?

(j) Why is it important to repeat an experiment several times before drawing conclusions?

(k) What is meant by the reliability of data? How can we check if data is reliable?

(l) What should a scientist do if the experimental data does not support their original hypothesis?

1.2 **(a)** What is the difference between a scientific theory and a scientific law?

(b) Discuss why scientific theories can change over time.

(c) Why did Dalton's model of the atom have to be changed?

(d) Explain what is meant by the term *science as a global enterprise*.

(e) Why is it important that scientists around the world follow the same rules and standards?

(f) Give two examples of how scientists achieve consistency in communication across the globe.

(g) What role does IUPAC play in international chemistry?

(h) Why do chemists use the SI system of units?

(i) What is meant by peer review? Explain why is it important in scientific publishing.

(j) Explain the term *repeatability* and give an example of when it is used in chemistry.

(k) What is reproducibility, and how does it differ from repeatability?

(l) Why is reproducibility especially important in the development of new drugs?

1.3 **(a)** 'Models link macroscopic observations with microscopic explanations.' Explain this statement.

(b) Explain why we need to use models in chemistry.

(c) Explain the term *scientific model*.

(d) What are the main purposes of using models in chemistry?

(e) Explain how using models can improve your thinking and visualisation skills.

(f) List three different forms a scientific model might take.

(g) In your own words, describe how models act as a 'bridge' between what we observe and what is really happening.

(h) Why is visual thinking important when studying chemistry?

(i) Describe how Molymod kits can help students understand chemical bonding.

(j) Give an example of a simplified representation in a model and explain its limitation.

(k) Why is it important to understand that models are only simplified versions of reality?

(l) Explain why scientific models may change or evolve over time.

(m) Give an example of how a model can be used to make a prediction in chemistry.

(n) How are computer simulations and mathematical models currently being used in climate science?

1.4 **(a)** Give three examples of how chemistry plays a role in maintaining or improving human health.

(b) Explain the role of chemists in drug design and development.

(c) What contribution did Alexander Fleming make to the fields of chemistry and medicine?

2 Atomic Structure: The Nuclear Model

2.1 Introduction

Many observations in chemistry suggest that the materials around us are made up of small particles. The scientific name for materials is **matter**. Thus, the idea that materials are made up of small particles is often referred to as the **particulate nature of matter**.

The term *particulate nature of matter* refers to the idea that all substances are made up of tiny, invisible particles. These particles can be atoms, molecules or ions, depending on the substance. We will explain the precise meaning of the terms *atoms*, *molecules* and *ions* later in this textbook. For the moment, just think of them as small particles. They are so small that we can't see them with our eyes.

The experiment shown in Figure 2.1 provides evidence for the existence of small particles.

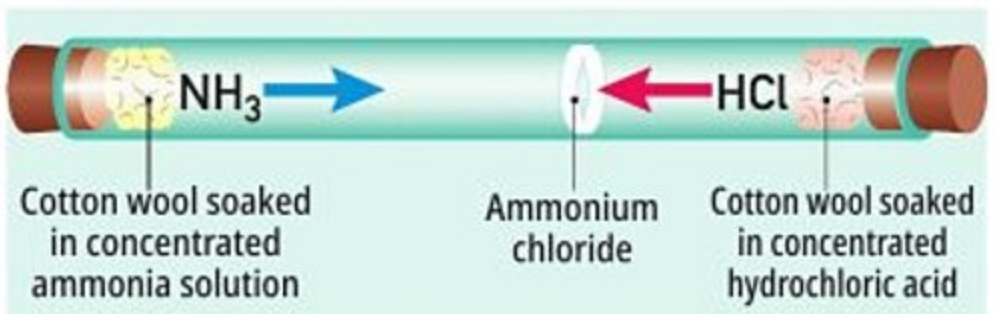


Figure 2.1 When the particles of ammonia gas meet the particles of hydrogen chloride gas, a white ring of a substance called ammonium chloride is formed.

The experiment may be explained as follows:

- Particles of the ammonia gas moving from left to right meet up with particles of hydrogen chloride gas moving from right to left. (Note that hydrochloric acid is a solution of hydrogen chloride gas in water.)
- A white, powdery substance (ammonium chloride) is formed where the particles of hydrogen chloride and ammonia meet.

OBJECTIVES

- To help students appreciate the key discoveries that led to our understanding of the nuclear model of the atom.
- To give students an understanding of how particles inside the atom (sub-atomic particles) are arranged in the nuclear model of the atom.
- To ensure that students know the properties of the proton, neutron and electron.

2.2 The development of the nuclear model of the atom

In this section, we will be quoting dates of various discoveries. You do not have to remember any of these dates. They are provided simply to give you an idea of when the work took place. There are lots of good videos available online to help you understand the experiments described in this section.

The Greek philosophers: Concept of the atom

Greek philosophers (about 400 BC) were the first to propose that matter was composed of small particles. The Greek philosophers believed that the tiny particles (of which all matter was composed) were so small that they could not be broken down into even smaller particles, i.e. they were indivisible. The Greek word for 'indivisible' is 'atomos', which gave us the word **atom** in the English language. You will have met the modern definition of an atom in your study of science at Junior Cycle level.

An **atom** is the smallest particle of an element that still has the properties of that element.

You will learn more about elements when you study the Periodic Table of the Elements.

Dalton's atomic theory

In 1808 an English chemist called **John Dalton**, Figure 2.2, wrote a book in which he put forward an Atomic Theory to explain the results of a number of experiments he had performed with gases.

The assumptions of **Dalton's Atomic Theory** may be summarised as follows:

1. All matter is made up of very small particles called atoms.
2. All atoms are indivisible. They cannot be broken down into simpler particles.

Figure 2.2
John Dalton
(1766–1844)
John Dalton proposed a theory about atoms in 1808. He thought of atoms as being like tiny snooker balls that cannot be broken down into simpler particles.

Just as snooker balls are solid and can't be easily broken apart, Dalton imagined atoms as small, solid spheres that cannot be broken down. Dalton wrote a lot more about his theory but the above two key points are the essential assumptions. However, Dalton's idea of the atom began to be questioned as a result of experiments carried out towards the end of the nineteenth century.

Discovery of cathode rays: William Crookes

In 1875 an English chemist called William Crookes, Figure 2.3, carried out experiments that involved passing an electric current through gases.

Figure 2.3
William Crookes
(1832–1919)
William Crookes investigated what happens when electricity is passed through gases.

Crookes used the apparatus shown in Figure 2.4 to pass the electric current through the air at low pressure. This type of glass tube is commonly called a vacuum tube. Crookes showed that rays were coming from the negative electrode (cathode) and that these rays cast a shadow of a Maltese cross at the far end of the tube. He used the name **cathode rays** to describe the rays coming from the cathode. In short, Crookes discovered cathode rays.

The cathode rays themselves are invisible – but when they strike the glass, they cause it to glow (or fluoresce), Figure 2.5. The shadow is caused when these cathode rays are stopped by the Maltese cross.

Crookes did not know that cathode rays consisted of tiny charged particles. This discovery was made by another scientist called J. J. Thomson.

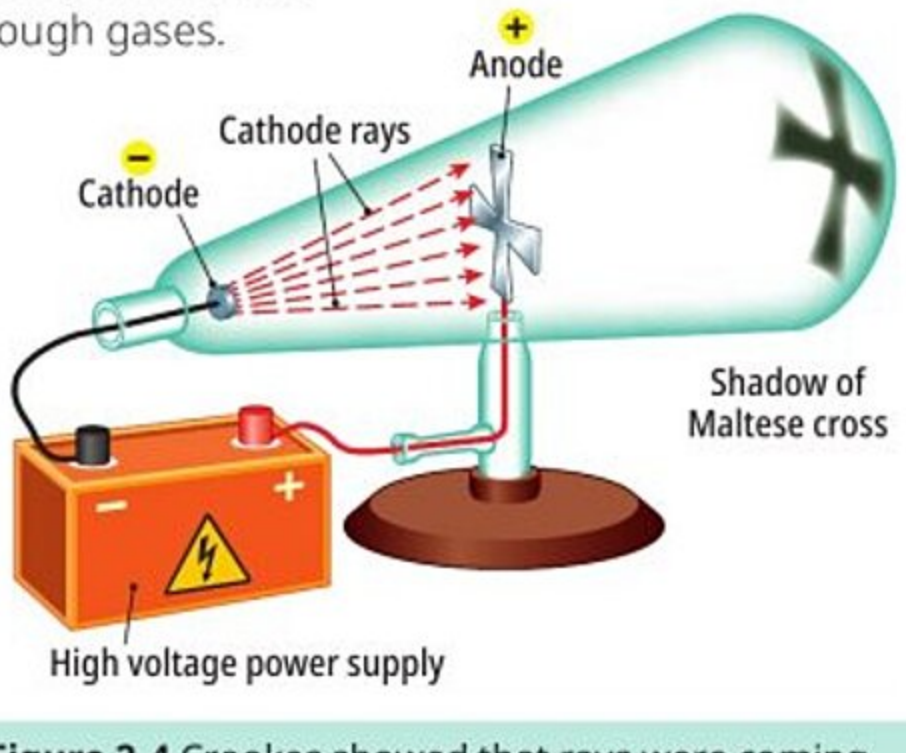


Figure 2.4 Crookes showed that rays were coming from the negative electrode (cathode) and that these rays cast a shadow at the far end of the tube. He had discovered cathode rays.

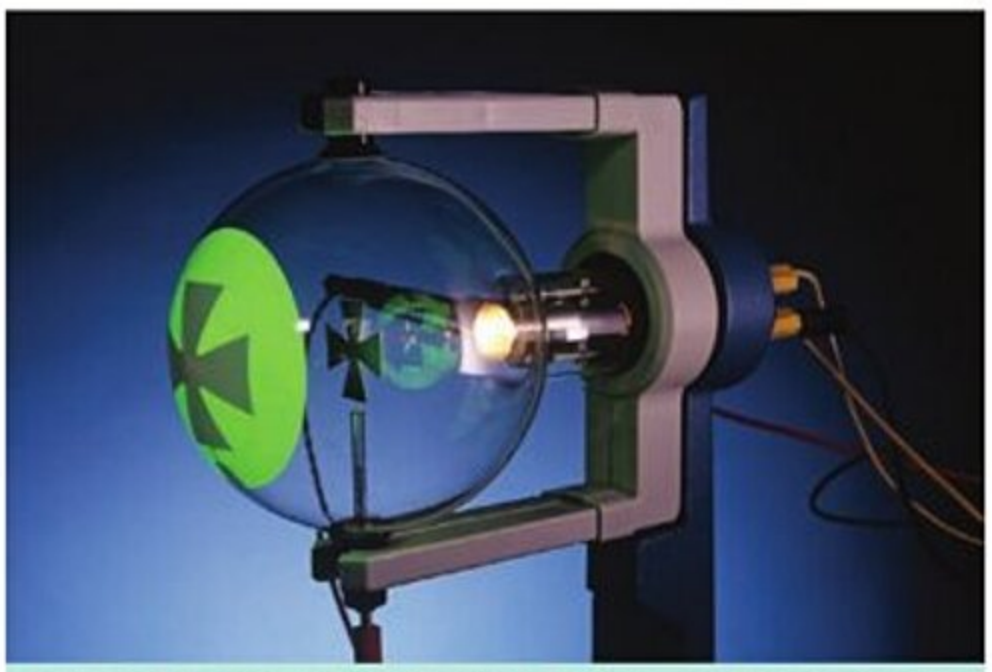


Figure 2.5 The shadow of the Maltese cross is caused by cathode rays being obstructed by the cross.

Discovery of the electron: J. J. Thomson

In 1897 an English scientist called **J.J. Thomson**, Figure 2.6, working in the Cavendish Laboratory at Cambridge University, devised an experiment to investigate if the cathode rays discovered by Crookes consisted of charged particles.

Figure 2.6

J.J. Thomson
(1856–1940)

J.J. Thomson is credited with the discovery of the electron. He received the Nobel Prize in physics in 1906 for his work on the electron.

Thomson's experiment may be summarised as follows:

- He produced a narrow beam of cathode rays by passing them through a small hole in the positive electrode, Figure 2.7.
- This narrow beam was passed between two parallel metal plates about halfway along the tube and then struck a fluorescent screen at the far end of the tube. This caused the fluorescent screen to glow.
- He found that when there was no charge on the parallel plates, the beam of cathode rays passed straight down the tube and struck the fluorescent screen at the position shown in Figure 2.7.
- On placing a positive charge on the top plate, the position of the spot moved upwards, as shown in Figure 2.8.
- Since the cathode rays were attracted up towards the positive plate, Thomson concluded that they consisted of negatively charged particles. (Unlike charges always attract each other.)
- The negatively charged particles are now called **electrons**.

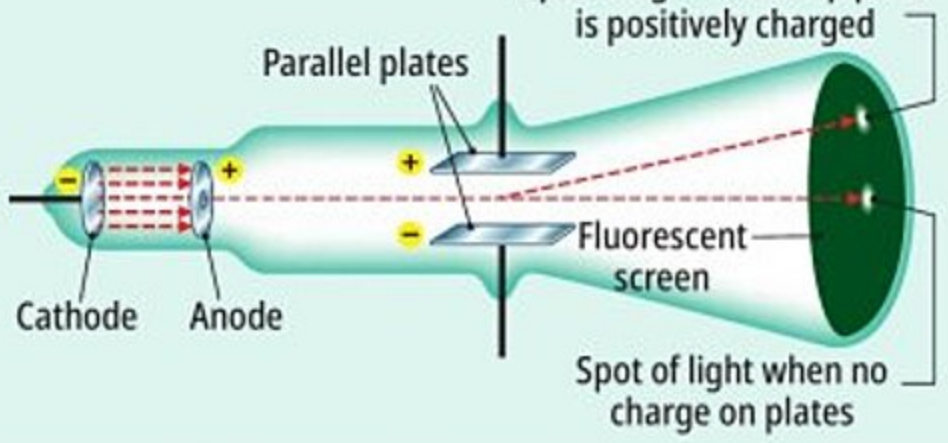


Figure 2.7 J.J. Thomson's apparatus proved that the cathode rays consisted of negatively charged particles.

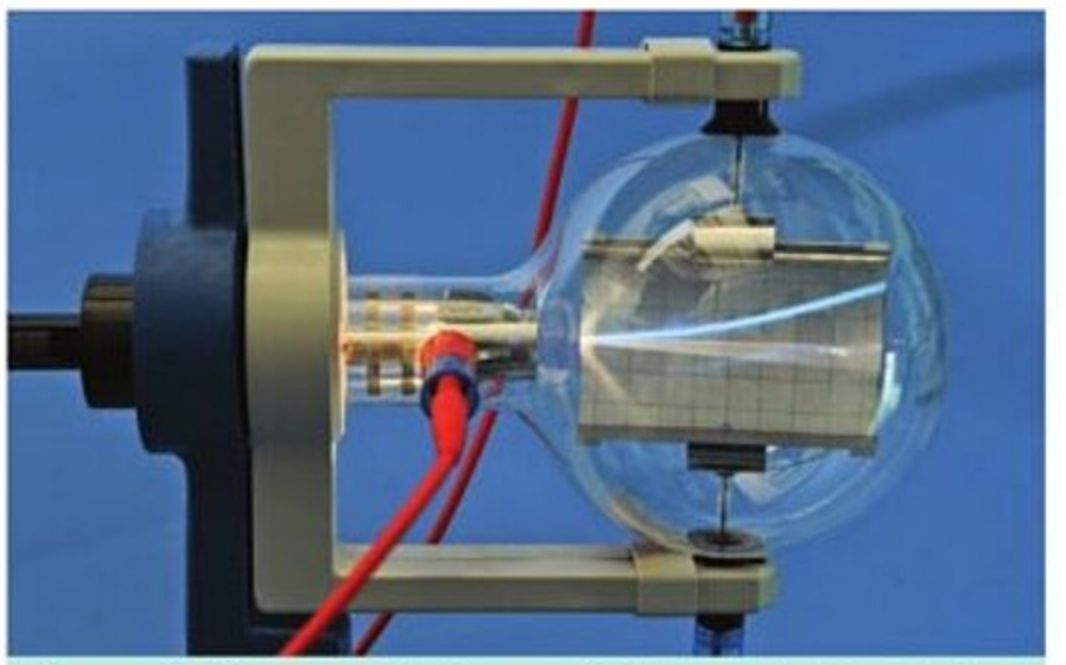


Figure 2.8 The negative beam of electrons is attracted up towards the positive plate. In this apparatus, fluorescent paper is used to show the path of the electron beam.

We now realise that what is actually happening in the above experiment is that the high voltage is 'dragging' electrons out of the atoms of the cathode. These electrons then travel towards the positive electrode. J. J. Thomson is recognised as the person who discovered the electron.

Cathode rays are streams of negatively charged particles called electrons.

From the results of his experiments, Thomson was able to measure the ratio of charge / mass of the electron.

In 1909 an American scientist called **Robert Millikan**, Figure 2.9, carried out a famous 'oil drop' experiment to determine the size of the charge on the electron. He found the value of the charge on the electron was 1.6×10^{-19} coulomb. (The coulomb is the unit of electric charge.)

Figure 2.9

Robert Millikan
(1868–1953)

Robert Millikan measured the size of the charge on the electron. He received the Nobel Prize in physics in 1923 for this experiment, which he carried out at the University of Chicago.

Since Thomson had measured the ratio of charge / mass of the electron, Millikan's discovery enabled the mass of the electron to be calculated as 9.1×10^{-31} kg.

Therefore, by 1909 the electron had been identified as a negatively charged particle of very small mass.

2.3 The 'plum pudding' model of the atom: J. J. Thomson

In 1898 J.J. Thomson proposed a very simple model of the structure of the atom. His assumptions may be summarised as follows:

- An atom is like a sphere of positive charge.
- Electrons are embedded in the sphere at random.

Since Thomson's model resembled a pudding with raisins in it or bits of fruit in a cake, his model of the atom became known as the 'plum pudding' model, Figure 2.10. His model did explain why atoms were neutral but Thomson did not have any experimental evidence to back up this simple model. The results of an interesting experiment performed in 1909 showed that Thomson's simple picture of the atom was **not** correct. This experiment is described in the next section.

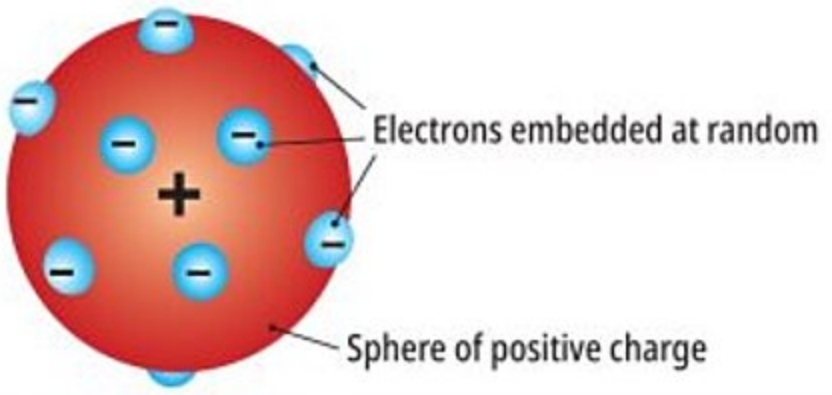


Figure 2.10 Thomson imagined an atom as a sphere of positive charge with negative electrons embedded in it at random. This model became known as the 'plum pudding' model of the atom.

2.4 The nuclear model of the atom: Rutherford

In 1909 a scientist from New Zealand called Ernest Rutherford, Figure 2.11, was working at Manchester University, England. Together with two research students, Rutherford studied the scattering of particles called alpha particles by a very thin sheet of gold foil. Alpha particles are positively charged particles produced by certain radioactive substances.

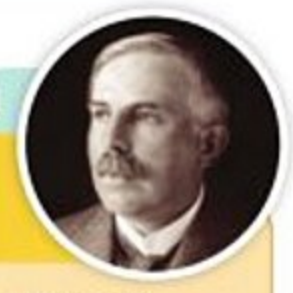


Figure 2.11

Ernest Rutherford
(1871–1937)

Ernest Rutherford received the Nobel Prize in chemistry in 1908 for his work on radioactivity. In 1909 he and his research team performed a very important experiment that led to the discovery of the nucleus.

A diagram of the experiment is shown in Figure 2.12 and may be summarised as follows:

- Rutherford bombarded a thin piece of gold foil with alpha particles.
- Alpha particles are positively charged and consist of groups of two neutrons and two protons stuck together, i.e. the nucleus of the helium atom. (You do not need to know any further information about alpha particles.)
- Rutherford used a phosphorescent screen to detect the alpha particles. A little flash of light appears on the screen when struck by alpha particles. The little flashes of light were observed through a microscope.

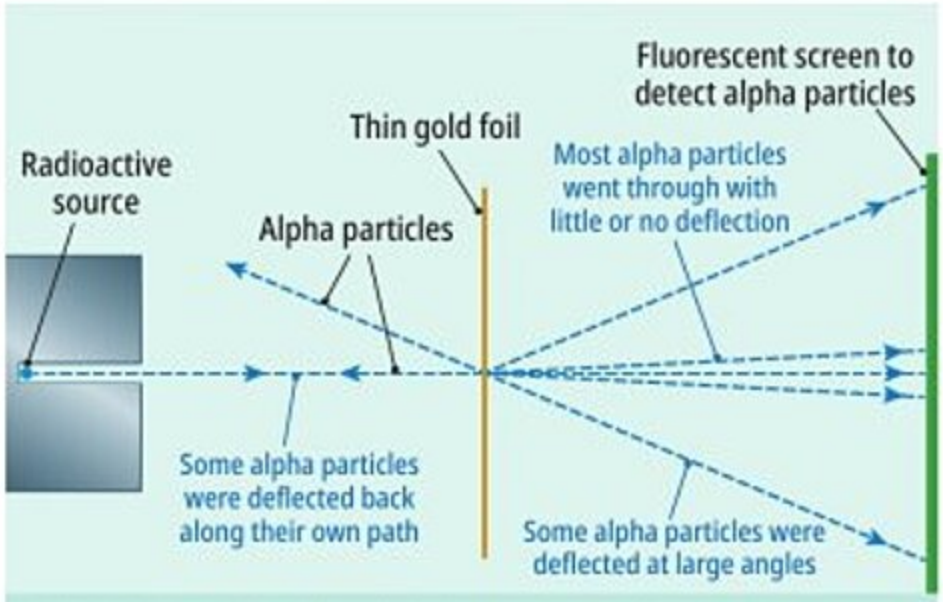

Fluorescent screen to detect alpha particles
Thin gold foil
Radioactive source
Alpha particles
Most alpha particles went through with little or no deflection
Some alpha particles were deflected back along their own path
Some alpha particles were deflected at large angles

Figure 2.12 The experiment carried out by Rutherford and his research team to investigate how alpha particles were scattered by a piece of gold foil

If Thomson's 'plum pudding' model of the atom were correct, then you would expect to find that some of the alpha particles would be deflected by small amounts. In other words, if the positive charge was distributed evenly throughout the atom, some of the alpha particles would suffer only slight deflections as they

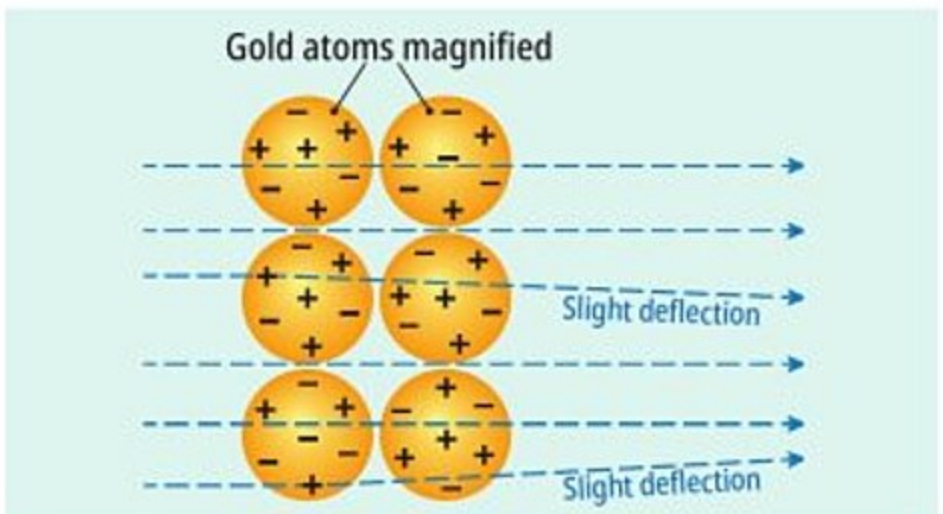


Figure 2.13 The expected result of the experiment if Thomson's model is correct. Most of the alpha particles should pass straight through the thin foil. Some alpha particles should suffer slight deflections.

passed through the atom. Most of the alpha particles should pass through undeflected, Figure 2.13.

Rutherford found that the vast majority of the alpha particles did indeed pass undeflected through the gold foil. Unexpectedly, however, some alpha particles were deflected at large angles as they passed through the gold foil. He also found that some alpha particles were deflected back along their own path. He did not expect these results, Figure 2.14.

Figure 2.14 Rutherford did not expect the alpha particles to be deflected at large angles and for some alpha particles to be deflected back along their own paths. He described it by saying that 'it was almost as incredible as if you fired a 15-inch shell at a piece of tissue paper and it came back and hit you'.

Rutherford concluded that the positive charge and the mass of the atoms of the metal foil were concentrated in a small dense core called the **nucleus** of the atom, Figure 2.15. It was clear that Thomson's 'plum pudding' model was not correct.

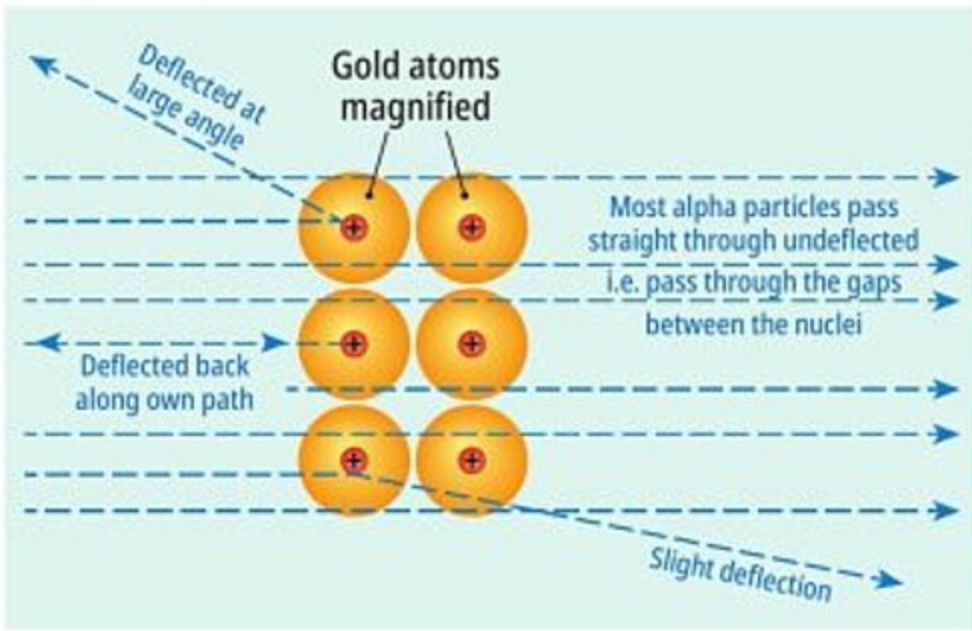

Deflected at large angle
Gold atoms magnified
Most alpha particles pass straight through undeflected i.e. pass through the gaps between the nuclei
Deflected back along own path
Slight deflection

Figure 2.15 The large deflections can be explained if the mass and positive charge of the atom are concentrated in a small core called the nucleus.

- The positively charged alpha particles and the positively charged nucleus repelled each other.
- Some alpha particles were reflected back along their original paths after colliding head on (a direct hit) with the nucleus.
- The deflection of the alpha particles at large angles was caused by the alpha particles coming very close to the high concentration of positive charge in the nucleus and being repelled by this high concentration of positive charge.
- Only a small number of alpha particles were reflected back along their original paths because the positive charge and the mass of the atoms of the gold foil were concentrated in such a small dense core (called the nucleus).
- From careful study of the scattering angles, Rutherford and his team deduced that the nucleus of an atom had a diameter of approximately $\frac{1}{100\,000}$ of the size of the atom. This explains why most of the alpha particles passed straight through the foil, because they never encountered the nucleus, i.e. most of the atom is empty space. If you could increase the size of the atom to that of Croke Park, the nucleus would be the size of a marble in the centre of the stadium.

The observations and conclusions of this experiment are summarised in Table 2.1.

Observation	Conclusion
Most alpha particles pass straight through the gold foil.	Most of the atom is empty space.
Some alpha particles are deflected at large angles.	The alpha particles are repelled when they pass near the small positive nucleus.
A small number of alpha particles are reflected back along their own paths.	A small number of alpha particles collide head on with the nucleus.

Table 2.1 Summary of some observations and conclusions from Rutherford's experiment.

There are some really good online videos that demonstrate Rutherford's experiment using modern apparatus. These videos are well worth watching.

2.5 Discovery of the proton

Rutherford and his research team continued bombarding various types of substances with alpha particles. They found that in the case of light atoms such as oxygen and nitrogen, small positively charged particles were given off as a result of the bombardment. Rutherford gave the name **proton** to these small positive particles.

This did not occur with the atoms of the heavier metals such as gold. They explained their results by saying that the alpha particles were breaking up the nuclei of the lighter atoms to release these positively charged particles. The reason that this did not occur in the case of the heavier gold atoms was because the large positive nuclear charge repelled the alpha particles before they had a chance to break up the nucleus.

2.6 Assumptions and limitations of Rutherford's nuclear model

Assumptions of Rutherford's nuclear model

1. Atoms contain a small, dense positive core called the nucleus. Most of the mass of the atom is concentrated in the nucleus.
2. Positive particles called protons are located in the nucleus.
3. The atom is mostly empty space.
4. Electrons are scattered around in the space surrounding the nucleus. This space is called the **electron cloud**. Rutherford proposed that electrons were moving around the nucleus but did not describe exactly the motion of these electrons.

The new structure of the atom proposed by Rutherford is illustrated in Figure 2.16.

Rutherford's nuclear model replaced the 'plum pudding' model and gave us a clearer understanding of the structure of the atom. The nuclear model was important, as it was the first time that scientists realised that the positive charge and most of the mass of the atom are concentrated in the nucleus of the atom.

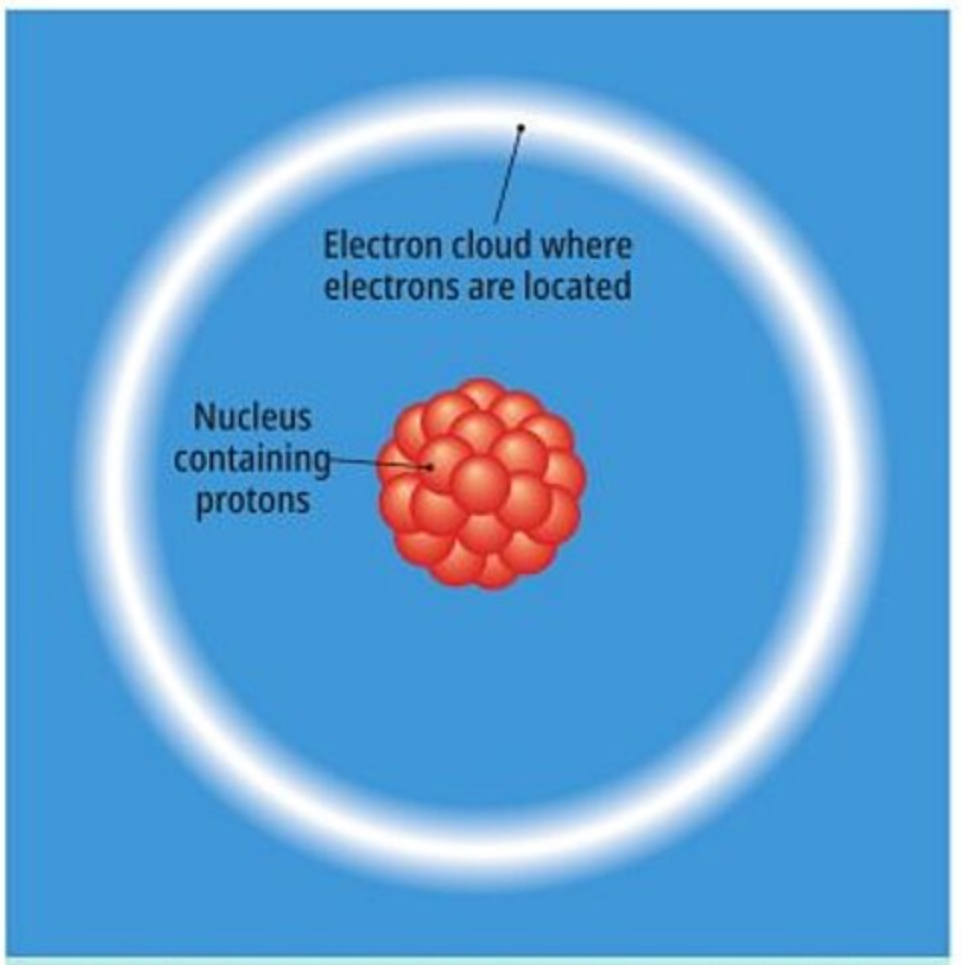


Figure 2.16 The model of the atom proposed by Rutherford consisted of a nucleus containing protons, with the electrons in an electron cloud surrounding the nucleus.

Limitation of Rutherford's nuclear model

1. Since like charges repel, why does the nucleus not fly apart due to the repulsion between the protons in the nucleus?
2. Since opposite charges attract, the model could not explain why electrons don't spiral into the nucleus. We know that this does not happen in real life as most atoms are stable.

We will discuss the explanation for these in the next chapter.

2.7 Discovery of the neutron

In 1932 James Chadwick, Figure 2.17, a student of Rutherford, carried out the following experiment:

- He bombarded a sample of beryllium with alpha particles, Figure 2.18.
- He discovered that some type of radiation consisting of particles with no charge came from the beryllium.
- The fact that the particles were neutral made them difficult to detect. Chadwick found that these neutral particles were penetrating enough to knock protons out of paraffin wax. This helped him to detect the neutral particles.
- He concluded that the alpha particles were knocking these neutral particles out of the nucleus of the beryllium atom.
- He found that these particles had about the same mass as the proton and, because they were neutral, he called them **neutrons**.
- Neutrons were discovered after electrons and protons because they were more difficult to detect since they are neutral.

After the discovery of the neutron, the nuclear model of the atom was more complete. Scientists now had a much clearer picture of the structure of the atom and the role played by neutrons. If it was only protons that existed in the nucleus, then the nucleus would fall apart because of the repulsive forces of the protons for each other (like charges repel). The neutrons help to 'cement' the positively charged protons together. After the discovery of the neutron, Rutherford's nuclear model of the atom was updated and is illustrated in Figure 2.19.

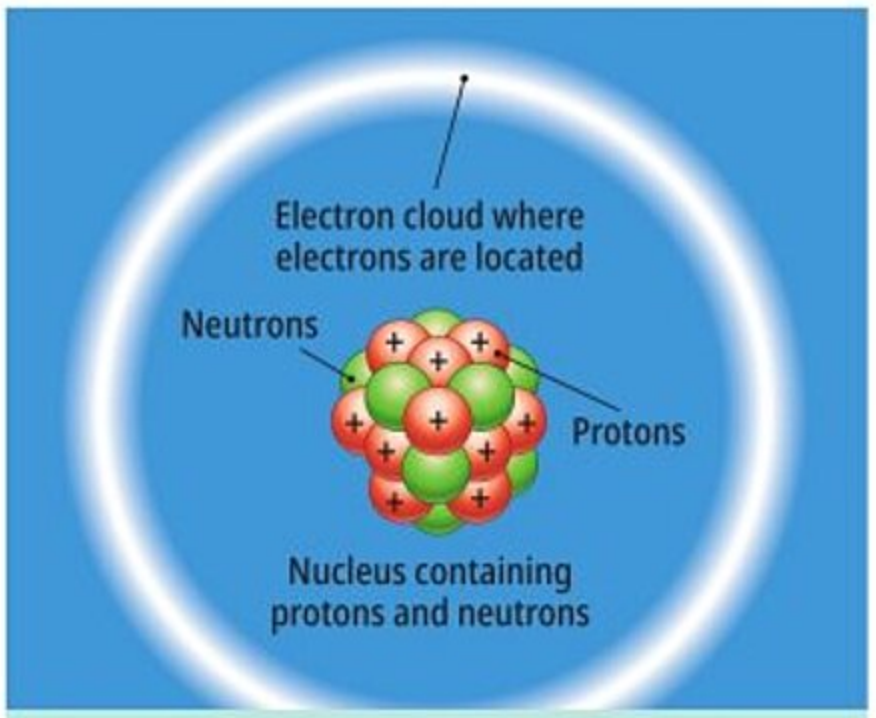


Figure 2.19 The updated nuclear model of the atom was an improvement on Rutherford's nuclear model, as it was now clear that the nucleus consisted of protons and neutrons.

Figure 2.17

James Chadwick
(1891–1974)

James Chadwick received the Nobel Prize in physics in 1935 for discovering the neutron.

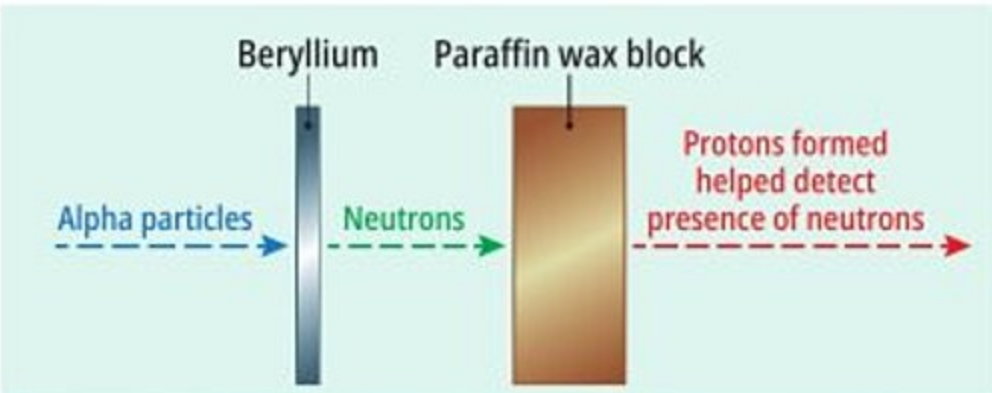


Figure 2.18 Alpha particles knocked neutrons out of the nuclei of beryllium atoms. Since neutrons have no charge, they were difficult to detect, so Chadwick used a piece of paraffin wax to detect them. The neutrons knocked protons out of the paraffin wax.

Assumptions of the updated nuclear model of the atom

The assumptions of the updated model of the atom may be summarised as follows:

1. Atoms consist of a small, dense positive core called the nucleus. Most of the mass of the atom is concentrated in the nucleus.
2. Positive particles called **protons** and neutral particles called **neutrons** are located in the nucleus.
3. The atom is mostly empty space.
4. Electrons are scattered around in the space surrounding the nucleus. This space is called the **electron cloud**. Rutherford proposed that electrons were moving around the nucleus but did not describe exactly the motion of these electrons.

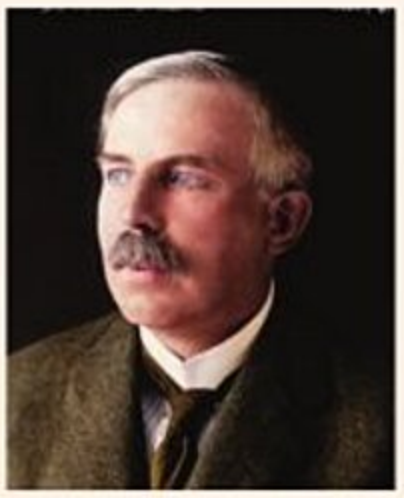
Limitation of the updated nuclear model of the atom

In the nuclear model, electrons are thought to move about in the space around the nucleus. However, since opposite charges attract, the electrons would lose energy and spiral into the nucleus, i.e. the atom would collapse. We know that this does not happen in real life, as most atoms are stable.

The fact that the nuclear model cannot explain how electrons stay in motion around the nucleus without crashing into it is a major limitation of the nuclear model.

Other limitations will be discussed in Chapter 3, when we study more modern ideas about the model of the atom.

SEC exam question 2.1



In 1911 Ernest Rutherford, a physicist from New Zealand, proposed the nuclear model of the atom. This model accounted for some of the properties of the atom.

Over the years it has been necessary, however, to modify and update the nuclear model, as new observations have been made. Describe the nuclear model of the atom.

The main points about the nuclear model of the atom may be summarised as follows:

- Atoms consist of a small, dense positive core called the nucleus. Most of the mass of the atom is concentrated in the nucleus.
- Positive particles called **protons** and neutral particles called **neutrons** are located in the nucleus.
- The atom is mostly empty space.
- Electrons are scattered around in the space surrounding the nucleus. This space is called the **electron cloud**.
- Rutherford proposed that electrons were moving around the nucleus but did not describe exactly the motion of these electrons.

EXAM TIP!

When providing a description, always break down the description into key points as shown above. It can also be helpful to include a labelled diagram (e.g. Figure 2.19 in this textbook) in case you leave out any key point in your description.

2.8 Properties of the proton, neutron and electron

With the discovery of the neutron, scientists were now aware of the existence of three particles inside the atom. These three particles are often referred to as sub-atomic ('inside the atom') particles. Protons and neutrons were located inside the nucleus and the electrons were located somewhere in the space outside the nucleus. (The location of the electrons is covered in more detail in Chapter 3.)

The charge on the electron was found to be -1.6×10^{-19} coulomb, the charge on the proton was $+1.6 \times 10^{-19}$ coulomb and, as we have seen, there was no charge on the neutron. The mass of the proton was found to be the same as the mass of the neutron, i.e. 1.67×10^{-27} kg. The mass of the electron was found to be much smaller at 9.1×10^{-31} kg. You are not required to remember any of these actual values but you should know the relative values as given in Table 2.2.

	Relative charge	Relative mass	Location
Proton	+1	1	Nucleus
Neutron	0	1	Nucleus
Electron	−1	$\frac{1}{1838}$	Outside nucleus

Table 2.2 Summary of the properties of sub-atomic particles.

TEST YOURSELF: Attempt Questions 2.1–2.4 and W2.1–W2.8.

Summary What I should know

- All matter consists of small particles.
- John Dalton said that all matter is made up of very small particles called atoms and that all atoms are indivisible, i.e. they cannot be broken down into simpler particles.
- Cathode rays are streams of electrons.
- J. J. Thomson showed that electrons are negatively charged and determined the charge to mass ratio of the electron.
- Robert Millikan measured the size of the charge on the electron using his 'oil drop' experiment.
- J.J. Thomson incorrectly suggested the 'plum pudding' model of the atom.
- The nuclear model of the atom emerged from Dalton's atomic theory and J.J. Thomson's 'plum pudding' model of the atom.
- Rutherford and his team discovered the nucleus of the atom and the existence of protons in the nucleus.
- James Chadwick discovered the neutron.
- Atoms contain a small, dense positive core called the nucleus. Most of the mass of the atom is concentrated in the nucleus.
- Positive particles called **protons** and neutral particles called **neutrons** are located in the nucleus.
- The atom is mostly empty space. Electrons are located in the space surrounding the nucleus called the **electron cloud**, which surrounds the nucleus.
- A limitation of the nuclear model is that it cannot explain how electrons stay in motion around the nucleus without spiralling towards the nucleus and crashing into it.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the meaning of the term *particulate nature of matter.*	⬡	⬡	⬡
Outline the experiments that led to the discoveries of the electron, proton and neutron.	⬡	⬡	⬡
Explain how Rutherford developed his nuclear model of the atom and how this was updated when the neutron was discovered.	⬡	⬡	⬡
State the properties of the proton, neutron and electron.	⬡	⬡	⬡
Evaluate the assumptions and limitations of Rutherford's original nuclear model of the atom and the updated nuclear model of the atom.	⬡	⬡	⬡

Chapter review questions

2.1 **(a)** What is meant by the term *particulate nature of matter*?

(b) Describe a laboratory experiment to demonstrate the diffusion of gases.

(c) Explain how this experiment is evidence for the particulate nature of matter.

2.2 **(a)** What is the scientific name for materials?

(b) The idea of atoms came originally from philosophers in a certain country. Name the country.

(c) State the two assumptions of John Dalton's theory about atoms.

(d) In 1875, I studied the discharge of electricity through gases using a glass tube containing a Maltese Cross. Who am I?

(e) What name is given to the rays coming from the electrode connected to the negative end of a discharge tube?

(f) J.J. Thomson showed that the rays coming from the negative end of a discharge tube were attracted towards a charged plate. What charge was on the plate?

(g) Name the American scientist who devised an experiment to measure the charge on the electron.

(h) Rutherford and his co-workers studied the scattering of certain types of particles by metal foils. What name was given to these particles?

(i) What type of particles did Rutherford and his co-workers use to knock protons out of the nuclei of some of the lighter elements?

(j) Name the scientist who discovered the neutron.

2.3 In 1909, Rutherford bombarded a very thin sheet of gold foil with alpha particles, most of which passed straight through it undeflected. Some alpha particles, however, were deflected at large angles and a very small number were reflected back along their original path. The first of these observations was not inconsistent with the 'plum pudding' model of the atom that had been proposed by Thomson in 1904, but Rutherford had to formulate a new model of atomic structure to account for the other two observations.

[LCH]

(a) What are alpha particles?

(b) Describe the structure of Thomson's 'plum pudding' model of the atom.

(c) Explain why some alpha particles were deflected at large angles as they passed through the gold foil.

(d) Why were some alpha particles reflected back along their original paths? Why did this happen to only a very small number of alpha particles?

(e) Draw a labelled diagram to show the new structure of the atom proposed by Rutherford.

2.4 **(a)** State the assumptions of Rutherford's nuclear model of the atom and draw a diagram to illustrate the new model of the atom proposed by Rutherford.

(b) Why did Rutherford's nuclear model play such an important role in our understanding of the structure of the atom?

(c) Discuss the limitations of Rutherford's nuclear model.

(d) What discovery by James Chadwick led to the realisation that Rutherford's nuclear model was an incomplete model?

(e) How does the updated nuclear model differ from Rutherford's nuclear model?

(f) State one limitation of the updated nuclear model of the atom.

2.5 Around 1909, Rutherford and his researchers bombarded thin gold foil with positively charged alpha particles from a radioactive radon-222 source and observed their resultant pathways. Most alpha particles passed through the foil with no deflection or very slight deflections, a small number were deflected through large angles, and a very tiny number rebounded back along their original paths.

(a) Based on the model of the atom that Thomson had proposed after his discovery of the electron in 1898, which one of these three observations was the most unexpected?

(b) What conclusion did Rutherford reach about the structure of the atom from all of the observations in the gold foil experiments taken together?

[LCH]

3 Atomic Structure: The Bohr and Orbital Models

3.1 Introduction

OBJECTIVES

- To give students an understanding of the Bohr and orbital models of the atom.
- To provide students with the opportunity to carry out laboratory investigations to identify elements.
- To help students discuss assumptions and limitations of models of the atom.

In the last chapter, we saw how the proton, neutron and electron were discovered. We studied how scientists found that the protons and neutrons were concentrated in the nucleus of the atom. The next question to be answered concerned the location of the electrons. Ernest Rutherford proposed that the electrons were located in some sort of electron cloud. However, he did not have a clear picture of their arrangement. It was a young Danish physicist called **Niels Bohr**, at the University of Copenhagen, who provided an insight into the arrangement of electrons in the atom, Figure 3.1.

Figure 3.1

Niels Bohr
(1885–1962)

Niels Bohr won the Nobel Prize in physics in 1922 for his study of the arrangement of electrons in the atom.

3.2 Bohr's study of spectra

Bohr developed a theory that explained the arrangement of electrons in atoms. In order to understand how Bohr developed his theory, we first need to study a few facts about spectra.

When white light (e.g. sunlight or light from an ordinary electric light bulb) is passed through a glass prism, the white light is broken up into an array of colours. Such an array of colours is called a *spectrum*, Figure 3.2. This spread of colours is referred to as a **continuous** spectrum, i.e. there are no gaps present in the spectrum. A rainbow is a common example of this type of spectrum. A rainbow in the sky is formed when raindrops act as tiny prisms and separate sunlight into its colours.

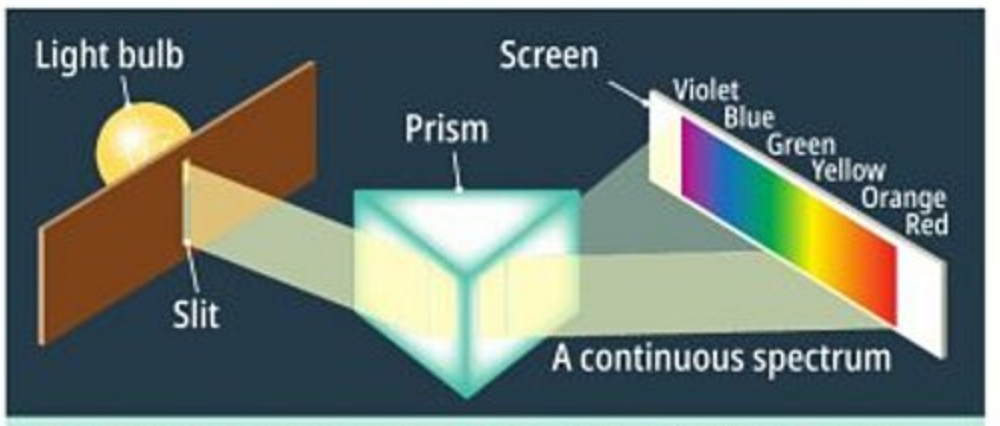


Figure 3.2 A continuous spectrum of colours from red to violet is formed when white light is passed through a glass prism.

You could repeat this using the light coming from a hydrogen discharge tube in place of white light. A hydrogen discharge tube is simply a glass tube filled with hydrogen gas at low pressure, through which an electric current is passed. Niels Bohr carried out this experiment and found that instead of seeing a continuous spectrum, he saw a series of narrow coloured **lines**, Figure 3.3.

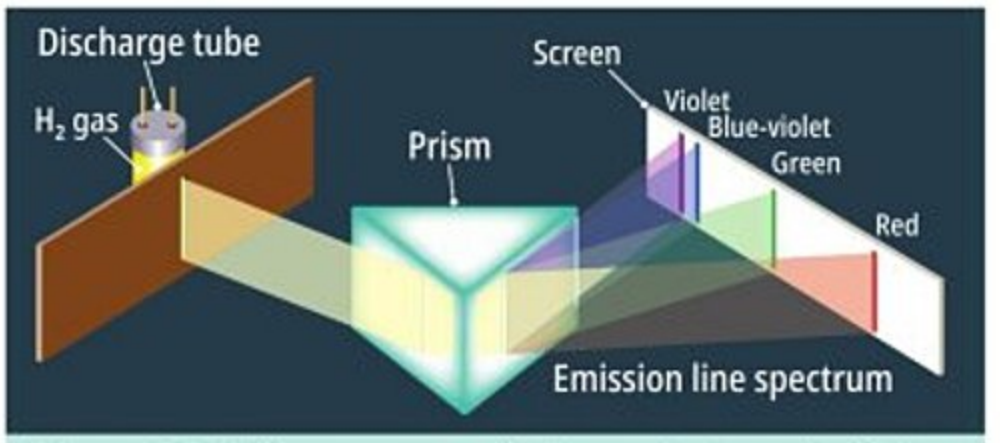


Figure 3.3 A line spectrum is formed when the light from a hydrogen discharge tube is passed through a prism.

Since the spectrum consists of lines, it is called a **line spectrum** to distinguish it from a continuous spectrum. Since the light is emitted when an electric current is passed through the hydrogen, the spectrum is more accurately called an **emission line spectrum**. This is also known as a **line emission spectrum**. Spectra are usually studied using an instrument called a spectrometer, Figure 3.4.

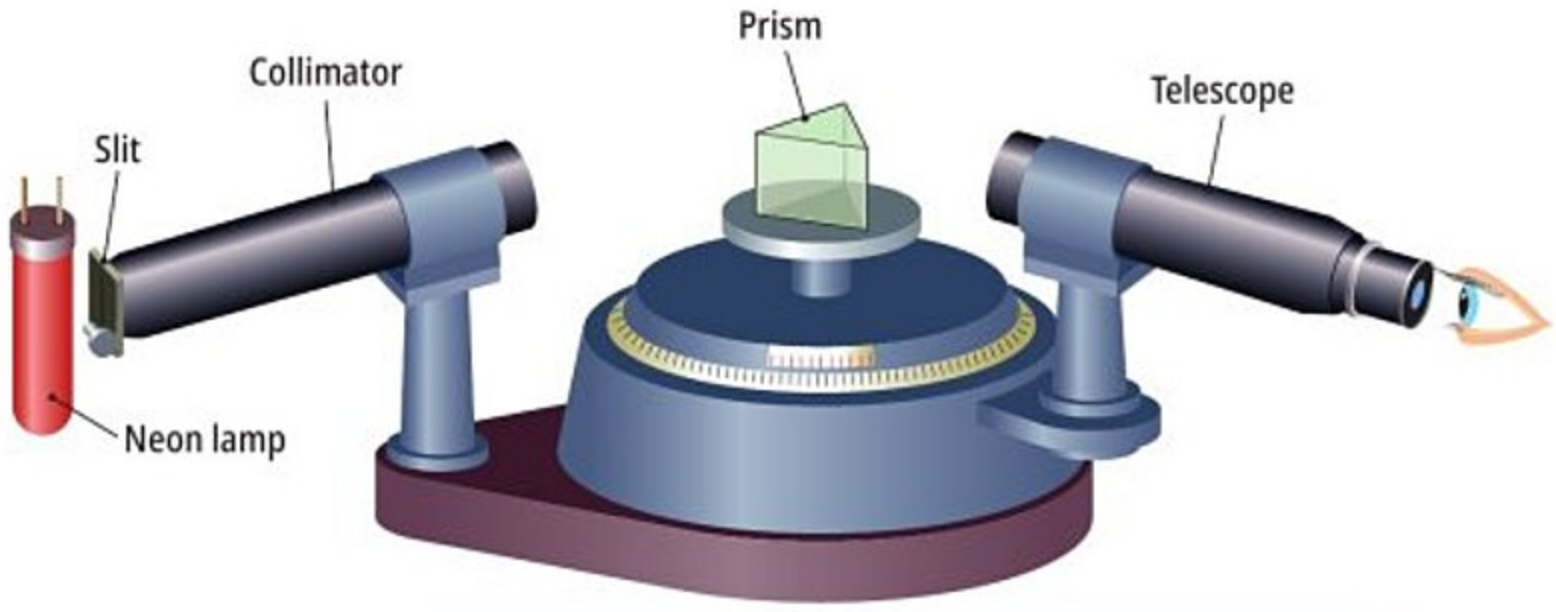


Figure 3.4 This instrument is called a spectrometer. In this diagram, it is being used to study the emission line spectrum formed by the light coming from the neon lamp.

When the light emitted by other elements (e.g. neon, sodium or mercury) was studied, it was found that these elements also produced line spectra.

Spectra are more easily studied in a darkened room. If you use a spectrometer to observe the light emitted by neon, you will see an emission line spectrum similar to that shown in Figure 3.5.

If you replace the neon lamp with a sodium lamp or a mercury lamp, you will see a different emission line spectrum for each of the elements, as shown also in Figure 3.5.

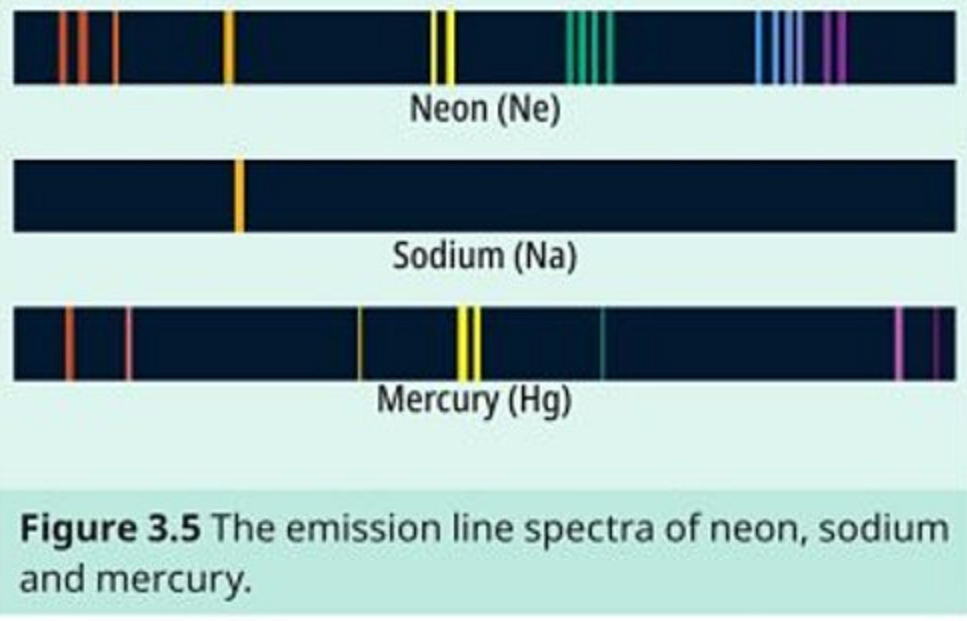


Figure 3.5 The emission line spectra of neon, sodium and mercury.

Note that each emission line spectrum is unique. These show how each element has its own unique emission line spectrum – a sort of 'fingerprint' of the element. In fact, the emission line spectrum of an element is often used by chemists to detect its presence. For example, in the analysis of steel, it is possible to detect the presence of various metals in the steel by studying the emission line spectrum obtained.

In our everyday lives, we observe the fact that different elements emit different colours when an electric current is passed through them. For example, sodium street lamps give off a yellow colour, mercury vapour lamps give off a blue colour and neon advertising signs glow red, Figure 3.6 a–c.

Figure 3.6a Sodium street lamps give off a yellow light.

Figure 3.6b Mercury vapour lamps give off a blue light.

Figure 3.6c Neon signs give off a red light.

If there is a spectrometer in your school laboratory, you may observe an emission spectrum of an element with it. If you do not have a spectrometer, you can observe an emission spectrum using a handheld spectroscope, Figure 3.7.

Figure 3.7 This scientist is studying an emission spectrum using a handheld spectroscope.

3.1 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 1 in the Student Laboratory Notebook.

Student Experiment No. 1

To carry out flame tests with salts of sodium, potassium, copper, lithium, barium and strontium

The main points of this experiment may be summarised as follows:

- Using a damp wooden splint, hold a sample of a sodium salt in the blue flame of a Bunsen burner.
- Repeat the procedure using salts of potassium, copper, lithium, barium and strontium.
- Each metal gives off a characteristic colour, Table 3.1.
- You can use the colours obtained to identify the metals present in unknown compounds.

Metal present	Colour
Sodium	Yellow
Potassium	Lilac
Copper	Blue-green
Lithium	Crimson
Barium	Green
Strontium	Red

Table 3.1 Colours given off by salts of various metals

Flame tests may be carried out using a wooden splint soaked in water or using a platinum wire. The splint or wire is dipped into a sample of the salt and held in the blue flame of a Bunsen burner. Some examples of flame tests for salts of these metals are shown in Figure 3.8.

DIGITAL: A video of this experiment is available on FolensHIVE.

Figure 3.8 A combination of six different flame tests obtained using a platinum wire

Note: There may be a slight variation in the intensity of the colour, depending on whether a wooden splint or a platinum wire is used. Also, in the case of copper, the balance between green and blue may vary depending on the copper salt used.

The various colours in fireworks displays are obtained by adding salts of various metals to the explosive mixture in the fireworks.

Identifying elements from their line emission spectra

In addition to identifying the elements studied in Experiment 1, for your exam you are also expected to be able to identify three elements from their line emission spectra. These three elements are sodium, strontium and copper.

You can identify the elements from data collected by yourself in the school laboratory (primary data) or from copies of spectra found in textbooks or other sources (secondary data).

Study Figure 3.9 a–c carefully to ensure that you can identify the spectrum if it appears on an exam paper!

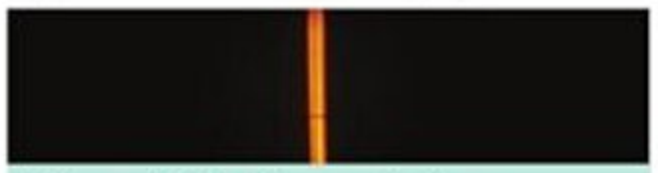


Figure 3.9a Line emission spectrum of sodium

Figure 3.9b Line emission spectrum of strontium

Figure 3.9c Line emission spectrum of copper

1. The line emission spectrum of sodium is the simplest of the three spectra as it consists of just a 'single' yellow line. (In fact, the single yellow line consists of two yellow lines very close together.) This accounts for the strong yellow light given off in the flame test for sodium.
2. The line emission spectrum of strontium has strong red lines on the right-hand side of the spectrum. These red lines are responsible for the red colour in the emission line spectrum of strontium.
3. The line emission spectrum of copper has strong blue and green lines on the left-hand side of the spectrum. These blue and green lines are responsible for the blue-green colour observed in the flame test for copper.

So far we have been discussing spectra and you may be wondering what this has to do with the structure of the atom. In fact, it was the study of emission spectra that led Niels Bohr to an understanding of how electrons are arranged inside atoms.

3.3 The Bohr model of the atom

Bohr realised that any model of the atom must explain two things:

1. Why are the emission spectra of the elements line spectra rather than continuous spectra?
2. Why is the emission spectrum of each element unique to that element?

These questions were answered by Bohr's Theory of Atomic Structure in 1913.

Prior to Bohr's theory, scientists thought that electrons in an atom could have **any** energy value. Bohr's Theory introduced the idea of **quantisation** of energy, i.e. that an electron in an atom can only have a fixed amount of energy. This fixed amount of energy is called a **quantum** of energy. Quantisation means that the energy of an electron in an atom cannot have just any value but is restricted to having only certain specific values (or levels), Fig 3.10.

Bohr suggested a way to relate the emission line spectrum of hydrogen to the structure of an atom of hydrogen. His research work is often described as providing 'spectroscopic evidence for the existence of energy levels'.

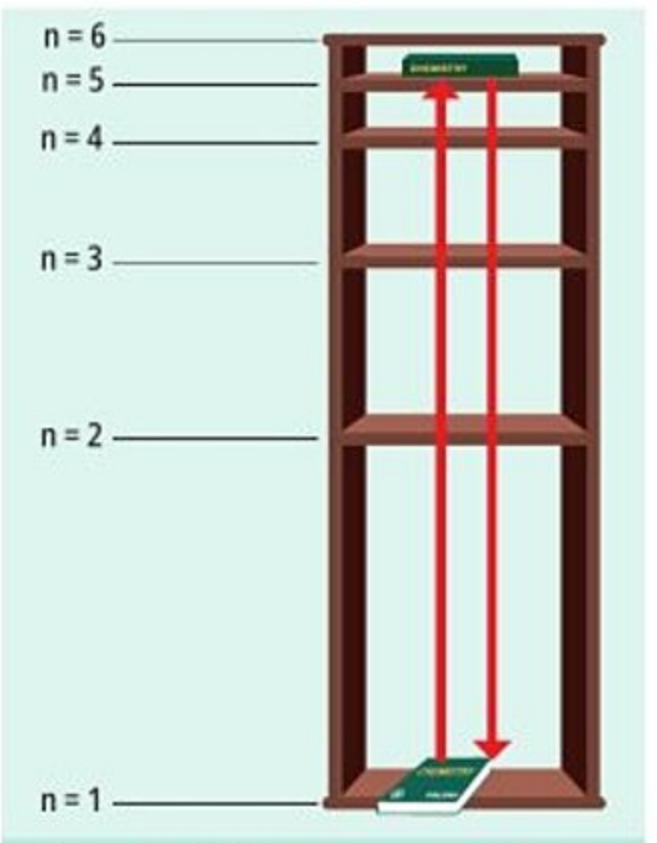


Figure 3.10 Electrons can only occupy certain energy levels. Each energy level has a fixed amount of energy associated with it. The book can only occupy certain shelves. Each shelf is a fixed distance from the ground and hence the book has a certain amount of potential energy on each shelf. Bohr's mathematical calculations showed that the energy levels became closer to one another as the value of n increased.

NOTE

Quantised means that the energy of an electron comes in fixed amounts. It's like stepping up a stairs instead of walking up a smooth ramp. As you stand on each step you have a fixed amount or 'chunk' of energy. In contrast, as you move up a smooth ramp, your energy increase is continuous.

Assumptions of Bohr's theory

- Electrons revolve around the nucleus in fixed paths called orbits.
- Electrons in any one orbit have a **fixed amount of energy**. Orbits are also called energy levels. (Orbits are also sometimes called 'shells' but this term is now rarely used.)
- Energy levels are represented by the letter *n*. The lowest energy level is the *n* = 1 level, the next highest is *n* = 2, etc.
- The energy of the electron in a particular orbit or energy level is **quantised**, i.e. fixed at a definite value.
- As long as an electron is in any one particular energy level, it neither gains nor loses energy. This helps to explain why electrons do not lose energy and fall into the nucleus.
- Atoms normally exist in the **ground state**, i.e. the electrons have the lowest amount of energy possible because they **occupy the lowest available energy levels**. For example, in the ground state of hydrogen, its single electron is in the lowest energy state (*n* = 1 energy level), Figure 3.11.
- Electrons in the ground state have energy of fixed values, i.e. the energy of the electrons in a particular orbit or energy level is fixed or quantised.
- In the **ground state**, the electrons occupy the lowest **available energy levels**.
- When an atom in its ground state is provided with energy (by electricity or heating), a **specific amount of this energy** is absorbed and the electrons **jump from lower energy levels to higher energy levels**. The electrons are now in an **excited state**.
- In some atoms of hydrogen, for example, the electron may move to the second energy level; in others, it may move to the third energy level.
- The **energy absorbed** is equal to the **difference in energy** between the lower energy level (ground state) and the higher energy level (excited state).
- Electrons in the excited state are unstable and they will fall back down to lower energy levels after a short period of time.
- As an electron falls from a higher energy level to a lower energy level, the excess energy is released in the form of a **photon** of light which has a definite or fixed amount of energy. (Sometimes the word 'discrete' is used instead of 'fixed'.)

An **energy level** is defined as the fixed energy value that an electron in an atom may have.

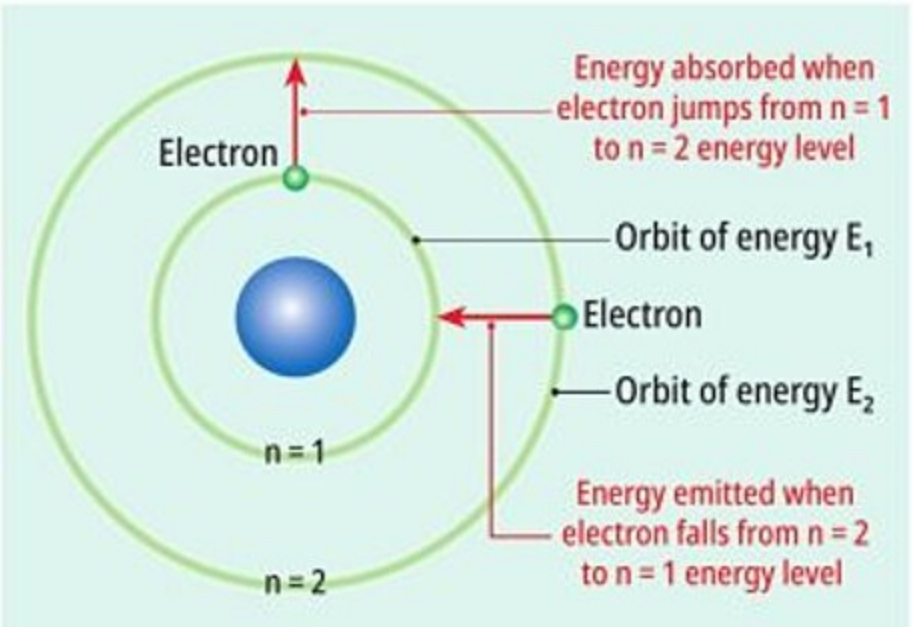

Energy absorbed when electron jumps from n = 1 to n = 2 energy level
Electron
Orbit of energy E_1
Electron
Orbit of energy E_2
n = 1
Energy emitted when electron falls from n = 2 to n = 1 energy level
n = 2

Figure 3.11 Bohr's Theory states that the energy of the electron in any one energy level is fixed or quantised. In the ground state of hydrogen, its single electron is in the *n* = 1 energy level. When a fixed amount of energy is absorbed, the electron moves to a higher energy level. The electron is now in an excited state.

The **ground state** of an atom is one in which the electrons occupy the lowest available energy levels.

The **excited state** of an atom is one in which the electrons occupy higher energy levels than those available in the ground state.

A **photon** is a fixed amount or 'packet' (quantum) of light energy or other forms of electromagnetic radiation.

Electromagnetic radiation is radiation such as visible light, infrared radiation and ultraviolet radiation.

- Since an electron can only fall back to certain definite energy levels, only fixed amounts of light energy can be given off, i.e. **light of a definite frequency is given off**.
- The frequency of the light emitted depends on the difference in energy between the two energy levels and is given by the equation $\boldsymbol{E_2 - E_1 = hf}$.
- E_2 represents the energy of the higher energy level, E_1 represents the energy of the lower energy level, *h* is a number that never changes called Planck's constant and *f* is the frequency of the light emitted.

The equation $E_2 - E_1 = hf$ tells us that the energy difference is proportional to the frequency of the light emitted, Figure 3.12.

- The definite amount of energy emitted (light of a definite frequency) appears as a line of a particular colour in the emission spectrum. Therefore, an emission line spectrum is formed.
- Since only definite amounts of energy are emitted, this implies that electrons can occupy only definite energy levels.
- Each definite amount of energy emitted gives rise to a line in the emission spectrum, Figure 3.13.

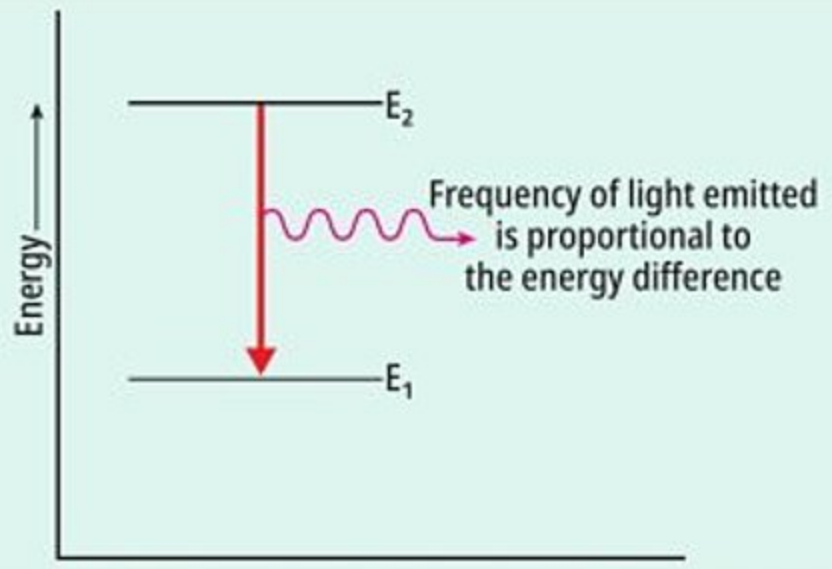
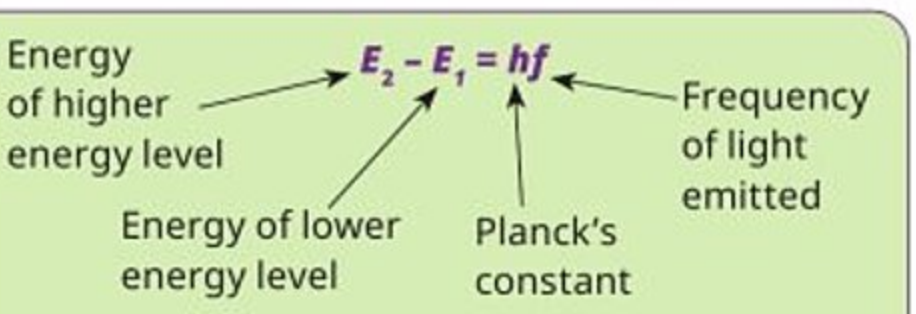


Figure 3.12 Energy is given out in the form of light of a definite frequency when an electron falls back from an excited state to a lower energy state.

EXAM TIP!

Study Figure 3.13 carefully. In past exam papers, questions were asked to relate a colour in the emission line spectrum to a particular transition. For example, be aware that the transition from n = 3 to n = 2 gives rise to a red colour.



The above equation may also be written as $E_m - E_n = hf$ where E_m is the energy of the higher energy level and E_n in the energy of the lower energy level.

- The series of invisible lines in the ultraviolet series (where electrons fall to the n = 1 energy level) is called the **Lyman series**.
- The series of lines in the visible spectrum (where electrons fall to the n = 2 energy level) is called the **Balmer series**.
- The series of invisible lines found in the infrared region (where electrons fall to the n = 3 energy level) is called the **Paschen series**.

These lines are named after scientists who first discovered the series of lines or studied them.

- Each element has a unique emission line spectrum because each element has a different number of electrons and has its own arrangement of these electrons in energy levels. Therefore, there will be different numbers and types of electron transitions for each element. These different electron transitions give rise to a different emission line spectrum for each element.

But is Bohr's theory correct? Bohr's work was of two kinds, both theoretical and experimental, and may be summarised as follows:

- Bohr realised that each coloured line in the emission spectrum of hydrogen has its own particular frequency.
- Firstly, he calculated mathematically the energy corresponding to each of the energy levels $n = 1$, $n = 2$, $n = 3$.

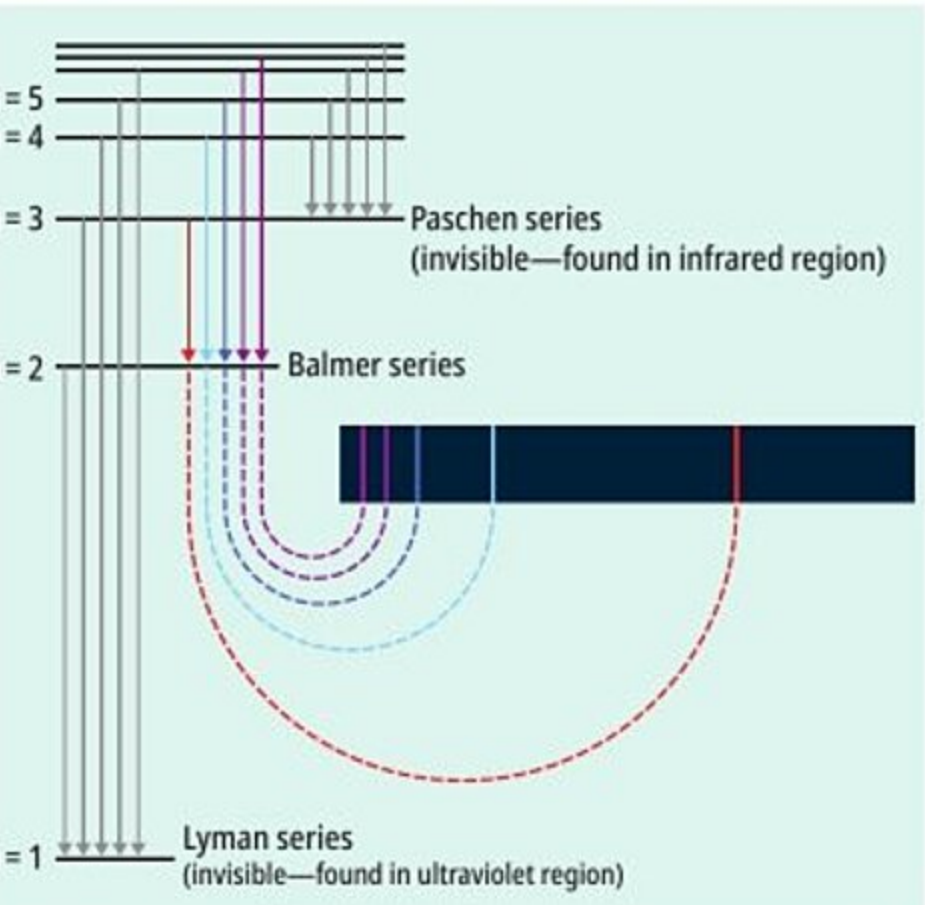


Figure 3.13 Each electron transition results in a line of particular wavelength in the emission spectrum of hydrogen.

EXAM TIP!

In a past exam paper, students were asked to explain why there is no yellow line in the hydrogen emission spectrum. The reason for this is because there is no electron transition in hydrogen that would give rise to an energy loss that corresponds to a yellow colour.

- Then he calculated the amounts of energy an electron would lose when falling from higher energy levels to lower energy levels.
- Finally, using the equation $E_2 - E_1 = hf$, he calculated the frequency and wavelength of the coloured lines corresponding to these electron transitions. (The above equation gave him the frequency and the equation *velocity of light = frequency × wavelength* enabled him to calculate the wavelength.)
- Bohr's experimental work involved him measuring the wavelengths of each line in the emission line spectrum of hydrogen using a spectrometer.
- He found that the wavelengths of light in the emission spectrum of the hydrogen atom calculated using his theory had exactly the same values as those measured experimentally, Figure 3.13.
- Therefore, the fact that only definite amounts of energy are emitted implies that electrons can only occupy definite energy levels, i.e. Bohr's suggestion that energy levels must exist in the atom was proven correct.

The three series of lines (Lyman, Balmer and Paschen) can all be satisfactorily explained on the basis of Bohr's theory. Bohr predicted their existence and their discovery added further credibility to his theory.

Students often ask the question: 'If the hydrogen atom has only one electron, why is it that so many electron transitions (as shown in Figure 3.13) are possible?' The reason for this is that even in a small sample of hydrogen, there are millions of atoms of hydrogen. When energy is supplied to the sample of hydrogen, not all atoms may receive exactly the same amount of energy. In some atoms, the electron may be promoted from the $n = 1$ to the $n = 2$ level, in others it may be promoted from the $n = 1$ to the $n = 3$ level, etc. Thus, when these electrons drop back down, they are coming from different energy levels and different lines will be formed in the emission spectrum since different electron transitions are involved.

Fluorescent light strips and lasers make use of electron transitions, Figure 3.14.

» Study Example 3.1 in the online resources.

TEST YOURSELF: Attempt Questions 3.1–3.2 and W3.1–W3.2.

NOTE

You may be wondering about the distinction between the words **spectrometer** and **spectroscope**:

- Instruments that are used to carry out **measurements** on spectra are called spectrometers, e.g. the instrument shown in Figure 3.4 can be used to measure wavelengths of light.
- Instruments that are simply used to **observe** spectra are called spectroscopes.

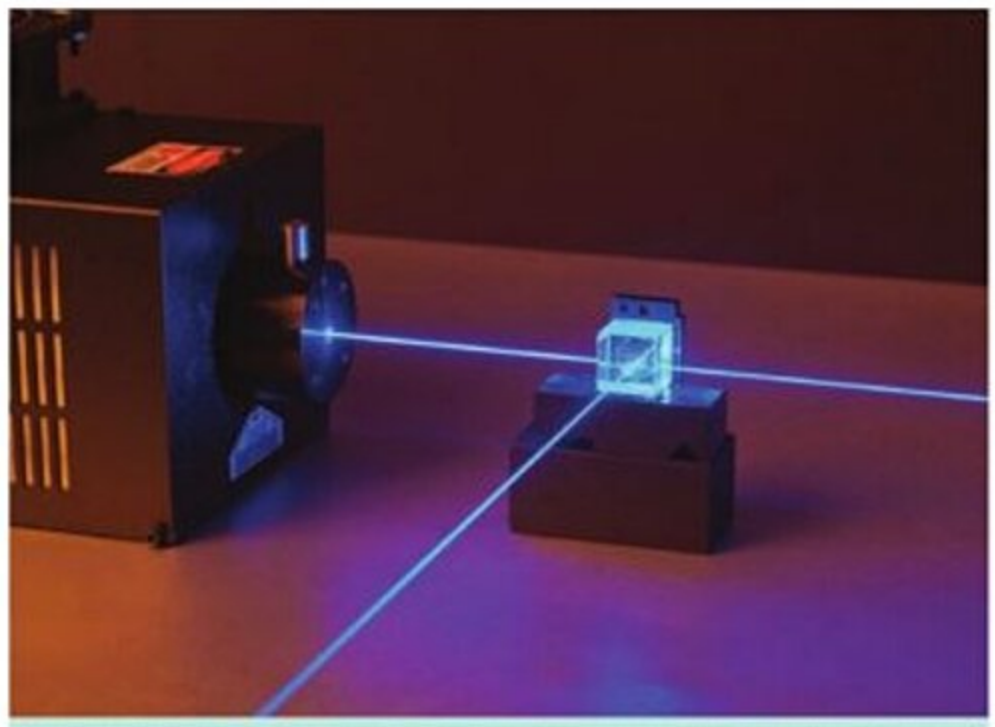


Figure 3.14 The light coming from this laser beam is caused by electrons falling from higher energy levels to lower energy levels.

3.4 Energy sublevels

As the study of spectra developed, more sophisticated spectrometers were becoming available. With these spectrometers, scientists were able to look more closely at lines formed in emission spectra.

Their work may be summarised as follows:

- In many cases, what appeared originally to be a single line actually consisted of a number of lines very close together. For example, in studying the emission spectrum of sodium, what appeared to be a single yellow line was found to be made up of two yellow lines very close together.
- These two lines could not have resulted from electrons dropping to two different energy levels as this would have given rise to lines much farther apart in the spectrum.
- To explain this observation, it was proposed that each main energy level, except the first, was made up of a number of sublevels, all of which were close in energy.

- From the analysis of spectra, it was discovered that the number of sublevels was the same as the value of *n* for the main energy level, i.e. the *n* = 2 main energy level had two sublevels, the *n* = 3 main energy level had three sublevels and the *n* = 4 had four sublevels, Figure 3.15.
- Scientists labelled the sublevels using the letters s, p, d and f. The sublevel of lowest energy was called the **s** sublevel, the one of next highest energy was called the **p** sublevel, the one above that the **d** sublevel and the one above that again was called the **f** sublevel. Note in Figure 3.15 that the 4s sublevel is in fact lower in energy than the 3d sublevel. This will be discussed in Chapter 4.

You might wonder why these particular letters were chosen to represent sublevels. Originally they were chosen from words used by scientists to describe lines in line spectra: s for 'sharp', p for 'principal', d for 'diffuse' and f for 'fundamental'.

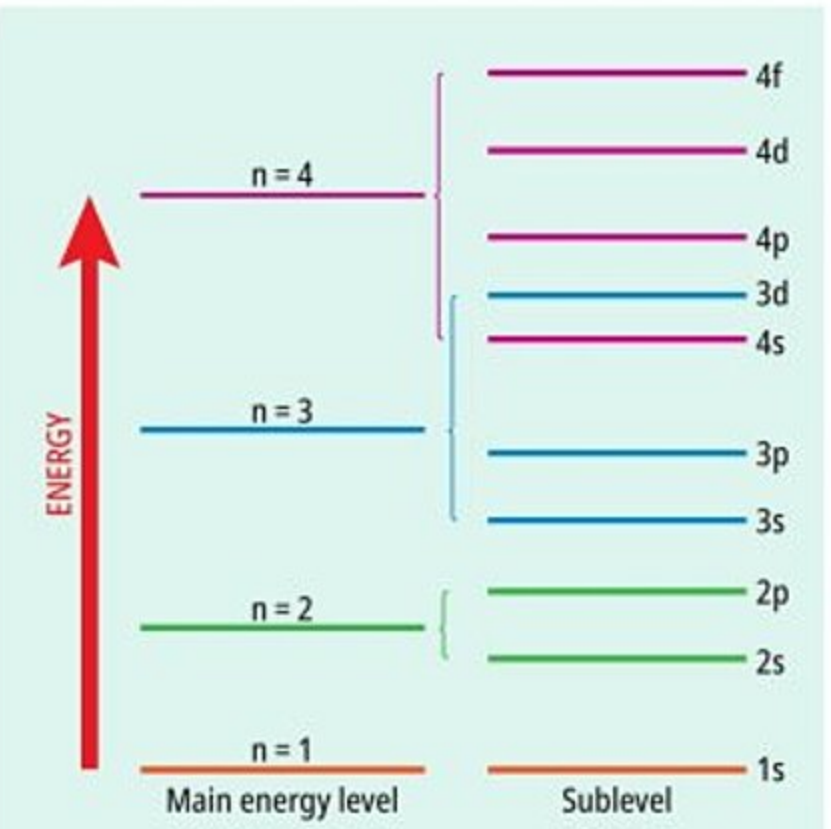


Figure 3.15 This diagram shows the sublevels associated with the main energy levels. Note that the 4s sublevel has been found to be lower in energy than the 3d sublevel.

3.5 Developments leading to changes in Bohr's model

We have already learned that Bohr proposed his model of atomic structure in 1913. However, in 1924 a French scientist called **Louis de Broglie** put forward a proposal that led to Bohr's model being questioned.

- De Broglie suggested that all moving particles have a wave motion associated with them.
- His calculations suggested that for fairly large objects such as a tennis ball, this wave motion would be impossible to detect. However, for a small object such as an electron, the wave motion should be possible to detect.
- De Broglie was proved correct in 1927 when it was discovered that moving electrons had a wave motion associated with them. This idea that a particle can behave like a wave is often referred to as 'wave-particle duality'.
- The discovery that electrons have a wave motion associated with them had major implications for the Bohr theory. If the electron has a wave motion, then Bohr's idea of an electron travelling in a fixed path at a precise, constant distance from the nucleus cannot be correct, Figure 3.16.

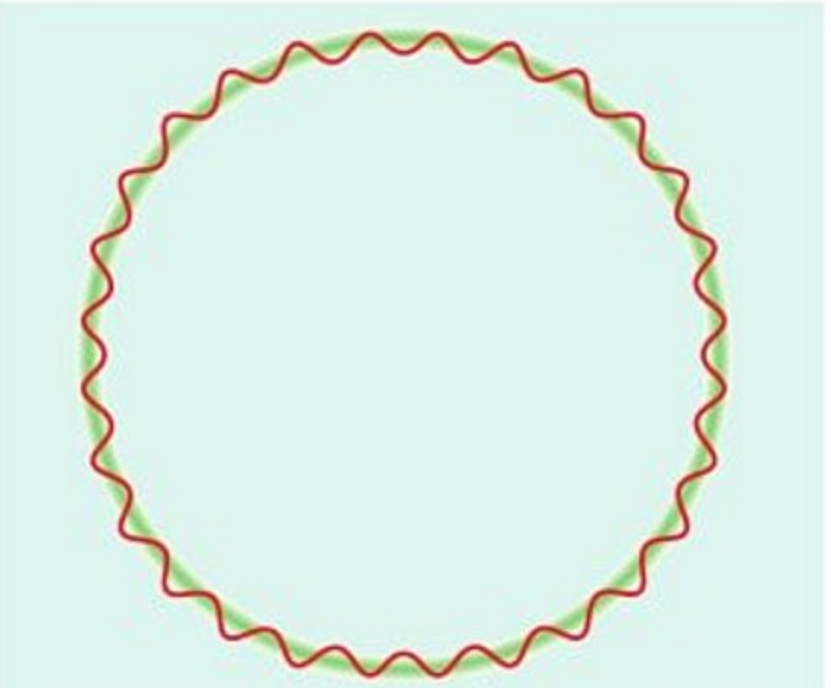


Figure 3.16 If the electron has a wave motion, then it cannot be travelling in a precise path at a fixed distance from the nucleus.

This problem was described mathematically by a German physicist called **Werner Heisenberg**, Figure 3.17.

He put forward a very famous principle called **Heisenberg's Uncertainty Principle**.

Heisenberg's Uncertainty Principle states that it is impossible to measure at the same time both the velocity and the position of an electron.

Figure 3.17

Werner Heisenberg
(1901–1976)

Werner Heisenberg was a German physicist who was awarded the 1932 Nobel Prize in physics for his famous uncertainty principle.

Heisenberg reasoned as follows:

- Consider a beam of light being used to detect the presence of an electron. The beam of light is like a radar signal that bounces off an object.
- When the beam strikes the electron, the position of the electron is determined – but since the electron has such a small mass, its velocity (speed) is immediately changed by the beam of light. So the act of trying to measure the properties of something so tiny, actually changes some of its properties.
- Heisenberg suggested that the Bohr picture of the atom was not completely satisfactory. Bohr's model visualised electrons moving with a certain speed in orbits of fixed distances from the nucleus.
- Heisenberg stated that you cannot say this about the electron since, for the reasons given above, you cannot measure at the same time both its speed and its distance from the nucleus (i.e. its location).

Heisenberg actually used the word *momentum* (mass × velocity) instead of *velocity* in stating his principle. However, since the mass of the electron is a constant value, and since we are not concerned with the mathematics of his principle, the simpler term *velocity* will be used here.

It was clear, therefore, that the idea of an electron moving in a fixed orbit around the nucleus had to be modified. If the electron is not travelling in a fixed path, then we can only talk about the **probability** of finding it at a particular position inside the atom.

This idea of probability led to a new picture being developed to describe the position of electrons in atoms and the limitations of Bohr's theory became clear.

Limitations of Bohr's model of the atom

1. Bohr's theory worked perfectly to explain the emission spectrum of hydrogen. However, when his theory was applied to atoms with more than one electron, it failed to account for many of the lines in the emission spectra of these atoms.
2. Bohr's theory did not take into account De Broglie's finding that electrons have a wave motion. Therefore, the idea of an electron travelling in a fixed path at a precise, constant distance from the nucleus cannot be true.
3. Bohr's model assumes that both the position of an electron (in an orbit) and its velocity are known precisely. However, Bohr's model is in conflict with Heisenberg's Uncertainty Principle which concluded that we can only refer to the **probability** of finding an electron in a region in space.
4. Bohr's theory could not explain the splitting of certain lines in emission spectra and did not take into account the presence of sublevels.

For many purposes in chemistry, the Bohr picture of electrons travelling in fixed paths around the nucleus is perfectly adequate. However, in some cases where we move more deeply into the subject, it is necessary to look at some modifications or changes to the Bohr model. This does not mean that the Bohr model is 'wrong'. The Bohr model works perfectly to explain some observations in chemistry. In other cases, we need a more modern model to explain our observations. We now study this more modern model.

SEC exam question 3.1

How did Niels Bohr modify the nuclear model of the atom?

Bohr modified the nuclear model of the atom put forward by Rutherford by proposing that:

- Electrons revolve around the nucleus in fixed paths called orbits.
- Electrons in any one orbit have a fixed amount of energy. Orbits are also called energy levels or shells.
- Energy levels are represented by the letter n. The lowest energy level is the $n = 1$ level, the next highest is $n = 2$, etc.
- The energy of the electron in a particular orbit or energy level is quantised, i.e. fixed at a definite value.

Note: The branch of science that explains how small objects such as atoms and electrons behave is called **quantum mechanics**. These small objects do not behave in the same way as large objects such as footballs or cars. Therefore, the orbital model of the atom is also called the Quantum Mechanical model of the atom.

3.6 The orbital model of atomic structure

Imagine that you are looking at an electron in an atom of hydrogen as it revolves around the nucleus. If you could take a large number of photographs of the electron and then put all of these photographs into one photograph, you would get a picture like that shown in Figure 3.18.

Note from the diagram that the shading is heaviest near the nucleus and gets less as you move away from the nucleus. This means that there is a high probability of finding the electron near the nucleus of the atom and the probability gets less as the distance from the nucleus increases.

Although diagrams such as that in Figure 3.18 give us a picture of the probability of finding an electron, they are quite tedious to draw. Instead, chemists draw a boundary within which there is a very high probability (approximately 95%) of finding an electron. The region within this boundary is called an **orbital**.

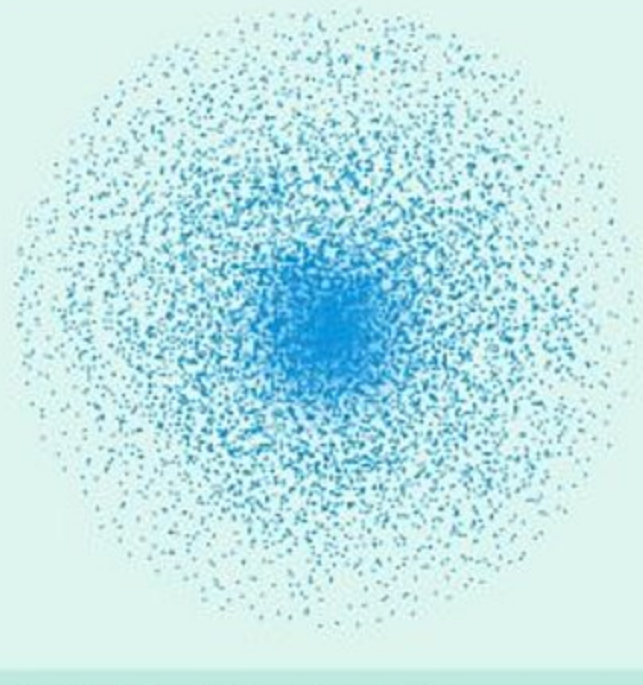


Figure 3.18 Diagrammatic representation of the position of an electron in an atom of hydrogen.

An **orbital** is a region in space within which there is a high probability of finding an electron.

EXAM TIP!

When defining an orbital, make sure you use the term *region* rather than *area*. As orbitals are three-dimensional, *area* is incorrect and will not be awarded any marks in an exam.

- The term *orbital* must not be confused with the term *orbit*. The term *orbit* was used by Bohr to describe the fixed path of an electron travelling with a certain velocity at a precise, constant distance from the nucleus. As indicated above, the term *orbital* was introduced to describe the more realistic probability picture.
- The orbital for the electron in a hydrogen atom in the ground state is called a 1s atomic orbital and is indicated in Figure 3.19.

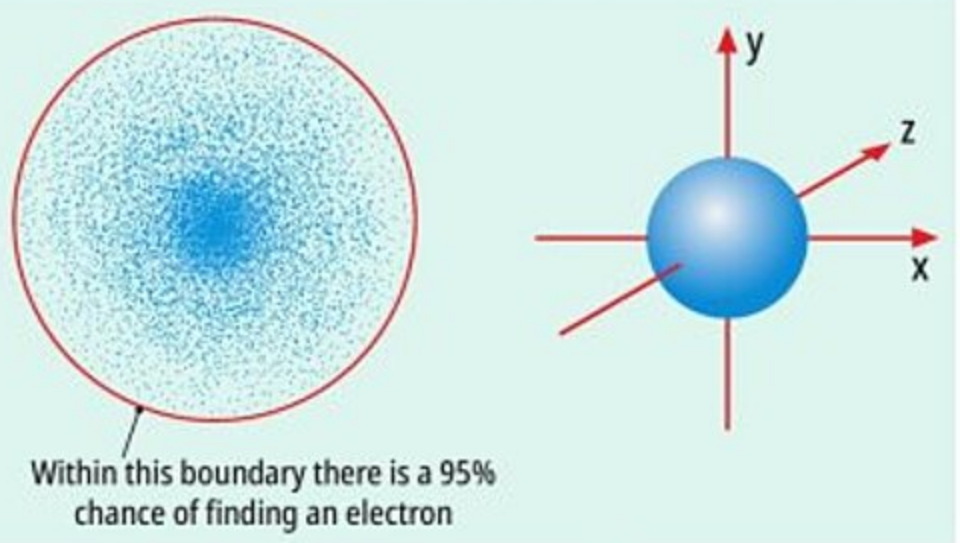


Figure 3.19 An s orbital is spherical.

The Austrian physicist **Erwin Schrödinger** devised mathematical equations to work out the probability of finding an electron in any particular sublevel in an atom, Figure 3.20.

Figure 3.20

Erwin Schrödinger
(1887–1961)

Schrödinger worked out the probability of finding a particular electron in an atom. It was his mathematical equations that gave us the shapes of orbitals. Schrödinger worked at the Dublin Institute for Advanced Studies for a number of years and became an Irish citizen.

Schrödinger's equations were solved and the solutions were plotted in three dimensions to give us the shapes of the four types of orbitals, s, p, d, and f. Thus, an orbital could also be described as a pictorial representation of the solution of the Schrödinger wave equation describing a particular electron.

- All s orbitals are spherical and differ only in size, Figure 3.21. In other words, the probability of finding an electron in a particular s sublevel is identical in all directions at a fixed radius from the nucleus.

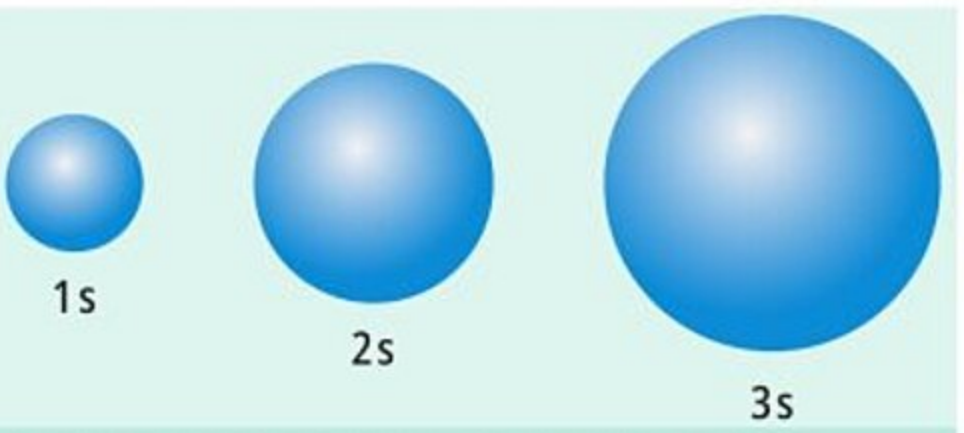


Figure 3.21 All s orbitals are spherical in shape.

When Schrödinger's equations were solved to describe the probability of finding an electron in a p sublevel, it was found that the resulting shapes resembled a dumbbell, i.e. **p orbitals are dumbbell-shaped**, Figure 3.22.

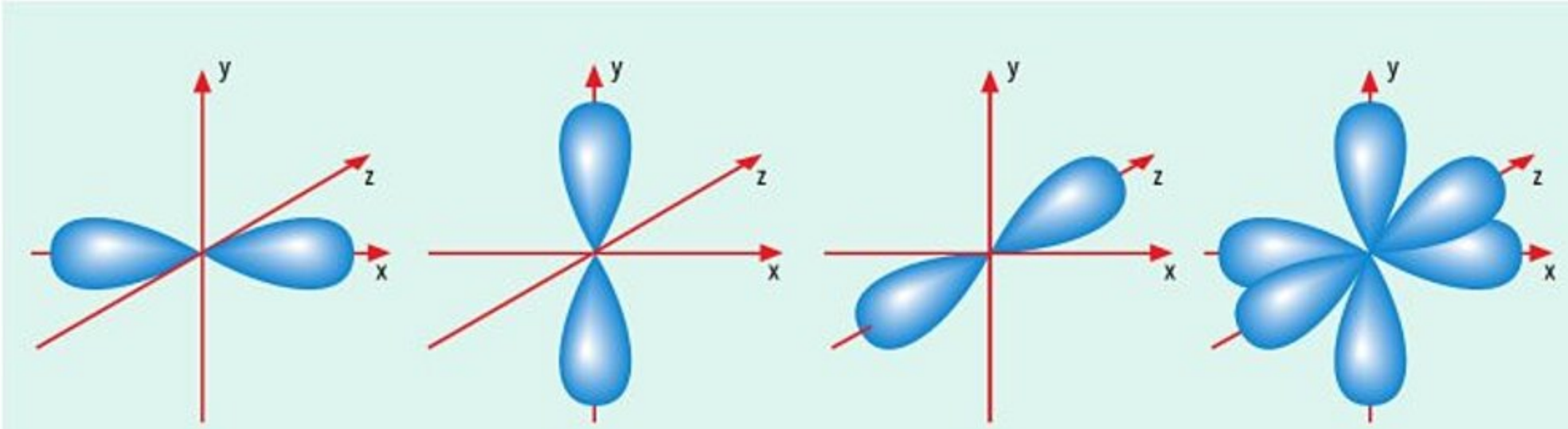


Figure 3.22 Note that p orbitals are dumbbell-shaped. Each p orbital points along one of the three main axes. Since the three axes are all at right angles to each other, it does not matter which is labelled x, y or z.

- It was discovered from the splitting of lines in emission spectra that each p sublevel consisted of three parts now denoted as p_x, p_y and p_z. The three corresponding p orbitals are of equal energy and only differ in their orientation in space as shown in Figure 3.22.
- The letters x, y and z stand for the three main axes to represent direction. The three p orbitals are therefore at right angles to each other. So, the probability of finding an electron in a p sublevel is represented by these dumbbell shapes.
- As one moves out from the nucleus along any of the x, y or z axes, the probability of finding an electron is shown by the shapes of the p orbitals. Within the boundary of the region enclosed by the dumbbell, there is a high probability of finding an electron. Outside the dumbbell, the probability of finding an electron is very low.
- Note that the 2s sublevel consists of one orbital (the 2s orbital). The 2p sublevel consists of three p orbitals all of the same energy. Thus, while the second energy level (n = 2) is divided into two sublevels (2s and 2p), overall there are four orbitals present (one s orbital and three p orbitals).

A **sublevel** is a subdivision of a main energy level and consists of one or more orbitals of the same energy.

We can now define a sublevel as follows:

The most modern model of atomic structure is the orbital model and this model is often seen as the foundation stone of modern atomic theory.

» Study Example 3.2 in the online resources.

In the next chapter, we will study how the electrons in atoms are distributed among the various orbitals.

TEST YOURSELF: Attempt Questions 3.3–3.5 and W3.3–W3.11.

Summary What I should know

- The formation of emission line spectra indicates the presence of energy levels in atoms. An emission line spectrum consists of coloured lines against a dark background.
- The instruments used to examine spectra are called spectrometers and spectroscopes.
- When metal salts are heated, different colours are emitted depending on the metal present in the salt.
- Bohr proposed that electrons revolve around the nucleus in fixed paths called orbits or energy levels.
- Bohr proposed that the energy of an electron in an energy level is quantised, i.e. has a fixed amount of energy.
- When an atom absorbs energy, electrons jump from a lower energy level to a higher energy level.
- Energy is lost when an electron falls from a higher energy level to a lower energy level.
- Since only definite amounts of energy are emitted, this implies that electrons can occupy only definite energy levels.
- Bohr's model of the atom has four main limitations.
- Heisenberg's Uncertainty Principle states that it is impossible to measure at the same time both the velocity and the position of an electron.
- An orbital is a region in space within which there is a high probability of finding an electron.
- s orbitals are spherical, p orbitals are dumbbell-shaped.
- A sublevel is a subdivision of a main energy level and consists of one or more orbitals of the same energy.

Learning outcomes

At the end of this chapter, I should be able to:			
Discuss how Bohr developed his theory to explain the arrangement of electrons in atoms.			
Investigate in the laboratory how flame tests may be used to identify certain elements in salts.			
Explain the assumptions of the Bohr model of atomic structure.			
Summarise the limitations of Bohr's model of the atom.			
Outline the work by De Broglie, Heisenberg and Schrödinger that led to the development of the orbital model of atomic structure.			
Evaluate in terms of assumptions and limitations the Bohr model of the atom against the orbital model of the atom.			

Chapter review questions

3.1 **(a)** Name the Danish scientist whose work provided much information about the arrangement of electrons in atoms.

(b) A rainbow of colours is obtained when white light is passed through a certain item. Name the item.

(c) What word is used to describe the fact that each element has its own emission line spectrum that is particular to that element?

(d) Name an instrument used to study spectra.

(e) What colour is given off when a sample of a salt of sodium is heated?

(f) An unknown salt when heated gave off a crimson colour. What metal is present in the salt?

(g) What is meant by the term *photon*?

(h) Bohr stated that the energy of the electron is quantised. What does this mean?

(i) What energy change takes place when an electron falls from a higher energy level to a lower energy level?

(j) In the equation $E_2 - E_1 = hf$ what does h stand for?

(k) Distinguish between the terms *ground state* and *excited state* of an atom.

(l) Explain why there is no yellow line in the hydrogen emission spectrum.

(m) Name the invisible set of lines in the ultraviolet region of the hydrogen emission spectrum.

(n) Why does sodium have a different line emission spectrum to copper?

(o) How would you distinguish between the emission line spectrum of strontium and that of copper?

3.2 **(a)** Indicate briefly how the study of spectra provided experimental evidence for the existence of energy levels in atoms.

What is meant by the *ground state* of an atom? [LCH]

(b) Distinguish between a continuous spectrum and a line spectrum.

(c) Fireworks displays often contain a wide range of different colours. How are these colours obtained?

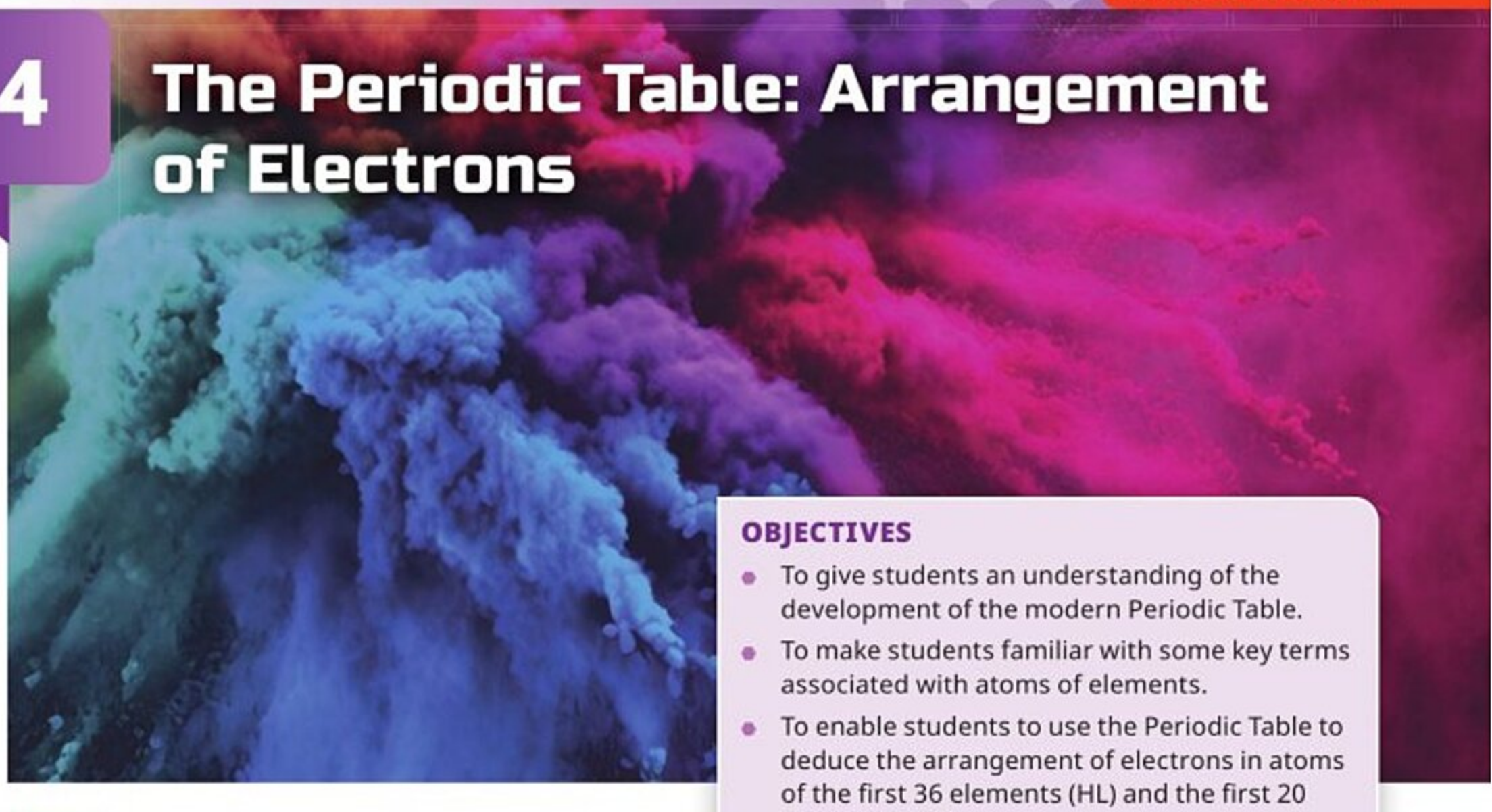
(d) Identify the element whose emission line spectrum is shown in Figure 3.25.

Figure 3.25

3.3 Distinguish between the terms *orbit* and *orbital*. Give a brief account as to why it was necessary for scientists to introduce the concept of the orbital. Your account should refer to the work of: (a) de Broglie, (b) Heisenberg and (c) Schrödinger.

Indicate using a diagram the difference between a 1s orbital and a 2s orbital.

4 The Periodic Table: Arrangement of Electrons



OBJECTIVES

- To give students an understanding of the development of the modern Periodic Table.
- To make students familiar with some key terms associated with atoms of elements.
- To enable students to use the Periodic Table to deduce the arrangement of electrons in atoms of the first 36 elements (HL) and the first 20 elements (OL).

4.1 Introduction

In this chapter, we will study one of the most important foundation stones in chemistry – the Periodic Table of the Elements. We will begin by discussing what an element is and consider some of the early ideas about elements. We will then look at the work of some chemists in trying to put these elements into some sort of order. The Periodic Table itself will then be studied, and we will learn how this table is of enormous help to us in deducing a whole range of information. Finally, we will learn how to use the Periodic Table to deduce how electrons are arranged in atoms.

4.2 The Elements

Greek philosophers had the idea that the universe was made up of a few basic substances or elements. These philosophers said there were four elements – earth, air, water and fire. Believe it or not, this idea remained the basis of chemical theory for almost two thousand years! There are two scientists who made a great contribution to the modern development of our understanding of the idea of an element.

An **element** is a substance that cannot be split into simpler substances by chemical means.

1. Robert Boyle

The first accurate definition of an element was given by an Irish chemist called Robert Boyle, Figure 4.1. In his book *The Sceptical Chemist*, published in 1661, he described an element as a simple substance that cannot be broken into anything simpler – a description that was broadly similar to the modern definition of an element.

Figure 4.1

Robert Boyle
(1627–1691)

Robert Boyle was the first chemist to properly define the meaning of the term *element*. He was born in Lismore Castle, Co. Waterford.

Copper is an example of an element. The modern definition means that whatever chemical reactions copper undergoes, you cannot split the copper into any simpler chemicals.

On the other hand, water is **not** an element because it can be split into hydrogen and oxygen. In fact, Boyle also predicted that elements combined together in chemical reactions to form what are now called **compounds**.

Chapter review questions

3.4 In 1885 the Swiss mathematician Johann Balmer wrote a mathematical formula to describe the wavelengths of the visible line spectrum of atomic hydrogen, which is now named after him. However, there was no explanation for the existence of these lines until 1913.

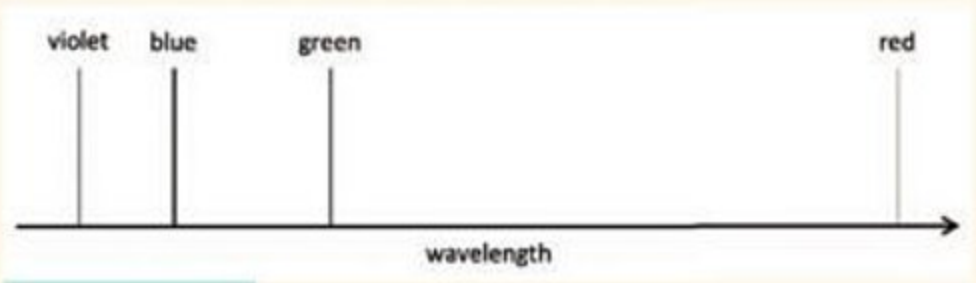


Figure 3.26

In 1913 Bohr's model of the hydrogen atom was shown to be consistent with the Balmer series.

Bohr's model was therefore supported by experimental evidence.

(a) (i) Bohr proposed that the electrons in an atom occupy energy levels.
Explain what is meant by the term *energy level*.

(ii) Distinguish between the ground state and the excited states of the electron in a hydrogen atom.

(iii) Explain what happens when an electron moves from an excited state to its ground state.

(iv) Name the instrument used to examine the line spectrum of an element.

In time, Bohr's model was shown to be an over-simplification of the structure of multi-electron atoms. Furthermore, modern atomic theory takes into account the wave nature of the electron and the Heisenberg Uncertainty Principle, which were not understood in 1913.

(b) (i) Explain how the Heisenberg Uncertainty Principle applies to an electron in an atom.

(ii) Draw the shape of a *p* orbital. [LCH]

3.5 **(a)** State two limitations of Bohr's theory that led to its modification. [LCH]

(b) Distinguish between an atomic orbital and a sublevel. [LCH]

(c) What does Heisenberg's Uncertainty Principle say about an electron in an atom? [LCH]

(d) Why is it possible for line emission spectra to be used to distinguish between different elements? [LCH]

(e) Figure 3.27 shows a building named after Erwin Schrödinger. What part did Schrödinger play in highlighting the need for the Bohr model of the atom to be modified?

Figure 3.27

2. Humphry Davy

Some of the most important discoveries in the history of the elements were made by an English chemist called **Humphry Davy**, Figure 4.2.

In 1807, at the age of 28 years, Davy discovered the element potassium by passing electricity through a compound of potassium.

Davy also discovered the elements sodium, calcium, barium, strontium and magnesium by passing electricity through compounds containing these elements. The discovery that an electric current could be used to obtain elements from their compounds was a turning point in the history of the discovery of the elements, Figure 4.3.

After 1807 many new elements were discovered. More than one hundred elements have been discovered to date.

Figure 4.2

Humphry Davy
(1778–1829)

Humphry Davy discovered many elements by passing electricity through their compounds.

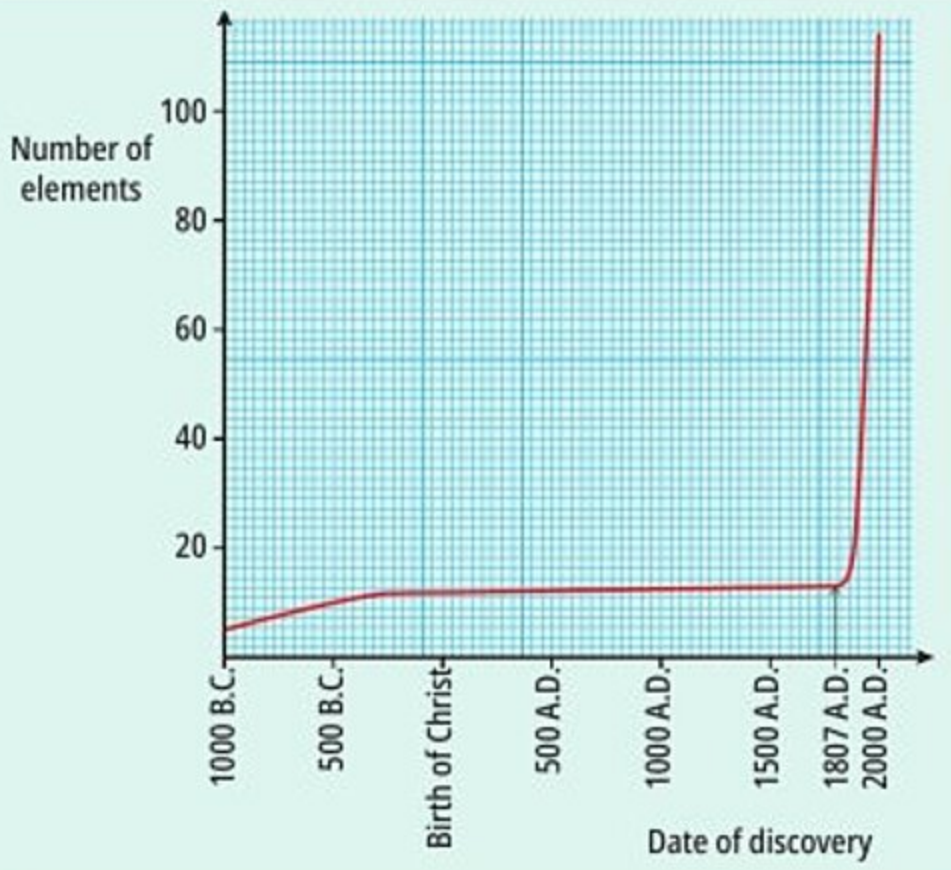


Figure 4.3 After Davy's discovery in 1807 that elements could be extracted from their compounds using electricity, there was a marked increase in the number of elements discovered.

4.3 The development of the modern Periodic Table

By 1800 approximately 35 elements had been discovered. As more and more elements were discovered, chemists were finding it difficult to understand and memorise the long lists of chemical and physical properties of these elements. They needed to find some kind of pattern or system to help simplify matters. It was the work of two chemists that eventually led to this pattern being developed. These two chemists were Dmitri Mendeleev and Henry Moseley.

Mendeleev's Periodic Table

- In 1869 Dmitri Mendeleev, Figure 4.4, professor of chemistry at the University of St Petersburg, Russia, wrote the properties of each of the 63 known elements on separate cards.
- He arranged these cards representing the elements in order of increasing atomic weight (relative atomic mass). We will study the meaning of this term later in this chapter.
- He placed elements with similar properties under each other in groups.
- He noticed a periodic repetition of properties, i.e. similar physical and chemical properties recurred at intervals. The word *periodic* means 'at regular interval'.
- He summarised his findings in what he called his 'Periodic Law'.

Mendeleev's Periodic Law: When elements are arranged in order of increasing atomic weight (relative atomic mass), the properties of the elements are repeated at regular intervals in other elements.

Figure 4.4

Dmitri Mendeleev
(1834–1907)

Dmitri Mendeleev arranged the elements in order of increasing atomic weight (relative atomic mass). His Periodic Table was quite similar to the modern Periodic Table.

Note: The repeating of properties at regular intervals is often referred to as a *periodic system*.

Mendeleev's work may be summarised as follows:

To demonstrate the regular repetition of properties, **he placed all known elements with similar properties in the same vertical column in a table**.

Because the properties of the elements repeated at regular intervals, or periodically, the table was called the **Periodic Table of the Elements**.

Mendeleev left gaps in his table. He had to do this to make all the known elements fit into the proper group (column) in terms of their properties, so that all elements with similar properties would be in the same column or group of the Periodic Table, Table 4.1. He said that the gaps represented elements that had not yet been discovered.

	Group I	Group II	Group III	Group IV	Group V	Group VI	Group VII	Group VIII
Period 1	H							
Period 2	Li	Be	B	C	N	O	F	
Period 3	Na	Mg	Al	Si	P	S	Cl	
Period 4	K	Ca	*	*	As	Se	Br	

Table 4.1 A section of Mendeleev's Periodic Table. The asterisks represent the gaps that Mendeleev left for undiscovered elements.

Mendeleev predicted the properties of undiscovered elements. Since he knew the properties of the other elements in a particular group, he was able to predict the properties that the undiscovered elements should have.

For example:

- He predicted that there would be an element discovered to fill the gap below silicon in Group IV of his table. He called this 'eka-silicon'. The element was discovered seventeen years later and called germanium (because it was discovered in Germany).
- He also predicted the discovery of an element to fill the gap below aluminium in Group III of his table. This element, which he called 'eka-aluminium', was discovered six years later and named gallium (because it was discovered in France – Gallia was the old Latin name for France), Figure 4.5.

When these elements were discovered, it was found that the properties predicted by Mendeleev were almost identical to the observed properties. These findings led to Mendeleev's Periodic Law being accepted.

You will notice in Table 4.1 that none of the noble gases in Group VIII are included. The reason for this is because Mendeleev did not suspect the existence of noble gases such as helium, neon and argon, as none of them had been discovered at the time.

Mendeleev reversed the order of some elements.

- In a few cases, he had to reverse the order of elements in order to make them fall into groups of elements with similar properties.
- If you look at the modern form of the Periodic Table (inside back cover) you will observe that tellurium (element number 52) is placed before iodine (element number 53). If you look at the atomic weight of tellurium you will observe that it is 127.6 whereas the atomic weight of iodine is 126.9.
- Since Mendeleev arranged the elements in order of atomic weight, originally he put iodine before tellurium. However, he realised that the properties were more important than the atomic weights and so he reversed the order of atomic weights for these two elements. This meant that each element would be in a group with elements of similar properties.
- By reversing the order, iodine is put in the same group as fluorine, chlorine and bromine – all of these elements have similar properties.
- Similarly, tellurium is put in the same group as oxygen, sulfur and selenium – again all of these elements have similar properties.

At last, order had been brought into the list of elements. In 1955 a newly discovered element (number 101) was named mendelevium in recognition of Mendeleev's enormous contribution to the study of the elements.

Figure 4.5 Mendeleev left gaps in his Periodic Table and predicted the discovery of germanium and gallium. Gallium has a low melting point. Note that the heat from the hand is melting the gallium.

The modern Periodic Table: Henry Moseley's contribution

We have seen that Mendeleev had to reverse the order of some elements. However, he did not understand the reason for this. It was an English scientist called Henry Moseley who provided the explanation, Figure 4.6.

Moseley studied the frequencies of the X-rays emitted by atoms of the different elements. In 1913 he found that the frequencies varied with the quantity of positive charge in the nucleus. In other words, he discovered a method of determining the number of protons in the nucleus of an atom. This number is called the **atomic number**.

Figure 4.6

Henry Moseley
(1887–1915)

Moseley developed a method of determining the atomic number of an element using X-rays. Sadly, he was killed in World War I at the age of 27.

The **atomic number** of an atom is the number of protons in the nucleus of that atom.

Moseley's discovery brought about a major improvement in Mendeleev's table. His work may be summarised as follows:

- Moseley showed that if the elements are arranged in order of increasing atomic number, it is not necessary to reverse the order of some elements as Mendeleev had to do.
- Moseley's X-ray studies showed that Mendeleev had been correct in placing tellurium (atomic number 52) before iodine (atomic number 53) in spite of the higher atomic weight of tellurium.
- Moseley showed that by arranging the elements in order of increasing atomic number the elements fall naturally into the correct groups in terms of their properties.

Moseley was the scientist who made the final step from Mendeleev's Periodic Table to the modern Periodic Table.

The **modern Periodic Table** is an arrangement of elements in order of increasing atomic number.

Thus, the modern version of the Periodic Law may now be stated as follows:

Modern Periodic Law: When elements are arranged in order of increasing atomic number, the properties of the elements are repeated at regular intervals in other elements.

Although Moseley's work did not alter Mendeleev's Periodic Table to a great extent, it certainly confirmed the position of the elements.

4.4 The modern Periodic Table

The main differences between Mendeleev's Periodic Table and the modern form of the Periodic Table (shown inside the back cover) are:

1 In the modern Periodic Table, the elements are arranged in order of increasing **atomic number**. In Mendeleev's Periodic Table, the elements are arranged in order of increasing **atomic weight** (relative atomic mass).

2. There are **more elements** in the modern Periodic Table. When Mendeleev constructed his table, some elements had not been discovered, e.g. the noble gases (group VIII or 18). There were only about 60 elements in Mendeleev's Periodic Table. There are over 100 elements in the modern Periodic Table.

3. There are **no gaps** in the modern Periodic Table. Mendeleev's Periodic Table contained gaps for undiscovered elements.

4. In the modern Periodic Table, **the transition elements are listed in a separate block** in the middle of the table. Mendeleev did not put these elements in a separate block. He included them with the other elements. In Table 4.1 the transition elements have been left out for clarity but, in fact, Mendeleev included copper in the same box as potassium, zinc in the same box as calcium, etc.

The differences between Mendeleev's Periodic Table and the modern Periodic Table are summarised in Table 4.2.

	Mendeleev's Periodic Table	Modern Periodic Table
1.	Elements arranged in order of increasing atomic weight (relative atomic mass)	Elements arranged in order of increasing atomic number
2.	Contains gaps for undiscovered elements	No gaps present
3.	Only 60 elements approximately, as not all elements had been discovered	Over 100 elements
4.	Transition elements were not put in a separate block	Transition elements are in a separate block

Table 4.2 Differences between Mendeleev's Periodic Table and the modern Periodic Table

There are some advantages of arranging the elements in order of atomic number:

- There is no need to reverse the order of some elements to force them into the correct groups.
- All of the elements are placed in groups with similar properties.
- To date, since all elements have been discovered up to element 118, there are no gaps in the modern Periodic Table.

The Periodic Table summarises an enormous amount of information and has brought order into chemistry. As chemistry students, you will find that it greatly simplifies your study of chemistry. You are allowed the use of a Periodic Table in the Leaving Certificate exam and it is included in the *Formulae and Tables* booklet approved for use in the state exams. We now consider three important uses of the Periodic Table: (i) obtaining atomic numbers and mass numbers, (ii) obtaining relative atomic masses and (iii) writing electron configurations.

So let's take a close look at each of these three uses.

4.5 Atomic numbers and mass numbers

We have already seen that the modern Periodic Table is an arrangement of elements in order of increasing atomic number. Therefore, the number of the element in the Periodic Table tells us the number of protons in the nucleus. For example, sodium is the eleventh element in the Periodic Table and therefore it has 11 protons in its nucleus.

Since the electron has such a small mass, its mass is ignored when calculating the mass of an atom. Therefore, almost the entire mass of an atom is due to the protons and neutrons in the nucleus of the atom. This allows us to define the mass number of an element as follows:

The **mass number** of an element is the sum of the number of protons and neutrons in the nucleus of an atom of that element

For example, sodium has 11 protons and 12 neutrons in its nucleus. Therefore, its mass number is 23 or we say that the mass of the atom is 23 atomic mass units. (Because the masses of atoms are so small, they are not normally measured in grams. A special unit is used called the atomic mass unit. The recognised symbol for atomic mass unit is **u** but in this textbook, for clarity, we shall use a.m.u. where 1 a.m.u. = 1.66×10^{-24} gram.)

The letter Z is used to indicate the atomic number.

The letter A is used to indicate the mass number.

The **nuclear formula** of an element is a method of summarising information about an element as shown in Figure 4.7.

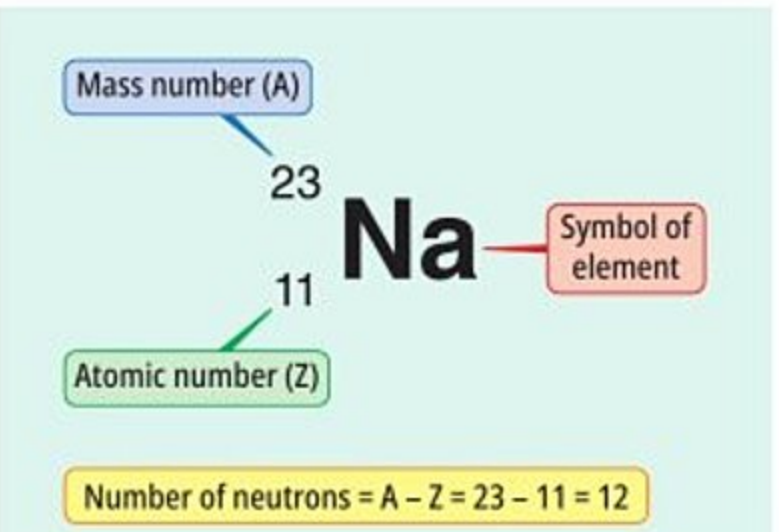


Figure 4.7 The nuclear formula for an element. To calculate the number of neutrons, simply subtract the atomic number from the mass number.

Note: The nuclear formula also contains the symbol of the element. For your exam, you must know the names and symbols of the first 36 elements.

- Note that in the nuclear formula, the atomic number is given at the bottom left hand corner near the symbol. However, in each box in the Periodic Table, the atomic number is given above the symbol. To avoid getting confused, remember that the smaller number is always the atomic number.
- Since the mass number is simply the number of protons plus neutrons, mass numbers must always be whole numbers.
- To obtain the mass number of an element from the Periodic Table, simply round off the number under the symbol to the nearest whole number. For example, for sodium, round off the 22.99 to 23. In fact, for most elements in the Periodic Table, you will observe the number under each symbol is not a whole number. This number is called the **relative atomic mass (atomic weight)** of the element. In the next section, you will learn what this number actually means.

Example 4.1

Question

How many (i) neutrons, (ii) electrons are in the ion $^{45}_{21}Sc^{3+}$? [LCH]

Answer

Number of neutrons = 45 – 21 = 24

Number of electrons in neutral atom = number of protons = 21

Since the atom has lost three electrons (ion is 3+)

Number of electrons = 21 – 3 = 18

Answer: (i) 24 neutrons, (ii) 18 electrons.

4.6 Relative atomic mass and isotopes

In 1919 an English chemist called Francis Aston, Figure 4.8, built an instrument called a mass spectrometer to measure the masses of atoms. Aston's work may be summarised as follows:

- He found that a sample of neon gas consisted of two varieties of neon atoms. One type of neon atom had a mass number of 20 and the other type had a mass number of 22.
- He concluded that the neon gas consisted of atoms of neon that differed in the number of neutrons in the nucleus $^{20}_{10}Ne$ and $^{22}_{10}Ne$.
- These two varieties of neon atoms are called **isotopes** of neon. The first isotope, $^{20}_{10}Ne$ has 10 neutrons in its nucleus. The second isotope, $^{22}_{10}Ne$ has 12 neutrons in its nucleus.
- Aston also identified two isotopes of chlorine: $^{35}_{17}Cl$ and $^{37}_{17}Cl$ commonly called chlorine-35 and chlorine-37.
- Carbon has been found to have three isotopes $^{12}_{6}C$, $^{13}_{6}C$, and $^{14}_{6}C$ which are commonly called carbon-12, carbon-13 and carbon-14, respectively.
- Hydrogen has been found to have three isotopes, as shown in Figure 4.9. Aston received the 1922 Nobel Prize in chemistry for his work on the discovery of isotopes.

Figure 4.8 Francis Aston built an instrument called a mass spectrometer. This instrument measures the masses of atoms. Aston was born near Birmingham, England.

Isotopes are atoms of the same element (i.e. they have the same atomic number) which have different mass numbers due to the different number of neutrons in the nucleus.

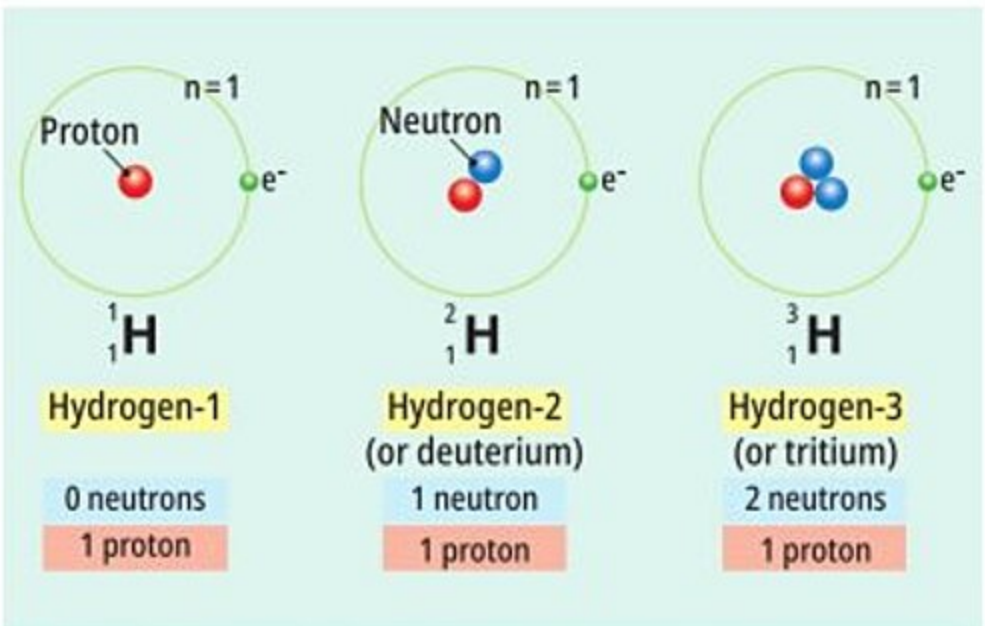


Figure 4.9 Hydrogen has three isotopes called hydrogen-1 (also called protium), hydrogen-2 (also called deuterium) and hydrogen-3 (also called tritium).

Not only did Aston detect the presence of isotopes but he also determined the percentages of each of the isotopes present in a sample of the naturally occurring element. For example, in his study of chlorine gas, he found that there were approximately three times as many chlorine-35 atoms as there were chlorine-37 atoms. He was then able to work out the average mass of an atom of chlorine. His method of calculation is shown in the following example:

Example 4.2

Question

A sample of chlorine is found to consist of 75% $^{35}_{17}Cl$ and 25% $^{35}_{17}Cl$. Calculate the average mass of chlorine atoms.

Answer

In 100 atoms of chlorine there are:

75 atoms of mass 35 = 75 × 35	= 2625
25 atoms of mass 37 = 25 × 37	= 925
Total mass of 100 atoms	= 3550
Average mass of 1 atom	= 35.5

From the above example, we see that the average mass of an atom of chlorine is 35.5.
If you locate chlorine in the Periodic Table, you will find that this is the number given under the symbol for chlorine. (To be more precise, it is 35.45 because the percentages have been rounded off in the above problem.) This 'average mass' of an atom is measured relative to the mass of the carbon-12 isotope. For this reason it is called its **relative atomic mass**. (The old name for relative atomic mass was **atomic weight**.) The symbol for relative atomic mass is $\mathbf{A_r}$.

Relative atomic mass is defined as:

- The average of the mass numbers of the isotopes of the element
- As they occur naturally.
- Taking their abundances into account and
- Expressed on a scale in which the atoms of the carbon-12 isotope have a mass of exactly 12 units.

Since relative atomic mass is a **ratio** of two masses, it has no units (i.e. the a.m.u. units above and below the line cancel out). Thus, we say that the average mass of an atom of chlorine is 35.5 a.m.u. but its relative atomic mass is 35.5.

Relative atomic mass $= \dfrac{\text{Mass of one atom of an element}}{\frac{1}{12}\text{ mass of one atom of carbon-12}}$

Example 4.3

Question

A mass spectrometer is used to analyse a sample of boron. It is found that the boron sample contains 18.7% $^{10}_{5}B$ and 81.3% $^{11}_{5}B$ Calculate the relative atomic mass of boron.

Answer

In 100 atoms of boron there are

18.7 atoms of mass 10 = 18.7 × 10 = 187	
81.3 atoms of mass 11 = 81.3 × 11 = 894.3	
Total mass of 100 atoms	= 1081.3
Average mass of 1 atom	= 10.813
i.e. relative atomic mass of boron	= 10.813

Uses of the mass spectrometer

Mass spectrometers are used to:

- Identify the presence of isotopes.
- Measure the relative abundances of isotopes.
- Measure relative atomic masses and relative molecular masses.
- Identify unknown compounds, Figure 4.10.

TEST YOURSELF: Attempt Questions 4.1–4.2 and W4.1–W4.3.

Figure 4.10 This mass spectrometer may be used to detect banned drugs taken by athletes and to test for drugs taken by drug addicts. Drugs leave traces in the hair of the addict. As hair grows about 1 cm per month, this test can reveal when the drug was last used. Hence, the success or failure of a rehabilitation programme can be monitored.

4.7 Arrangement of electrons in atoms

We have already learned that Niels Bohr proposed the idea of electrons revolving around the nucleus in fixed paths called orbits or energy levels. The arrangement of electrons in an atom (i.e. the number of electrons in each main energy level) is called the **electron configuration**.

The **electron configuration** shows the arrangement of electrons in an atom of an element.

If we use the Periodic Table, it is very straightforward to write the electron configuration of an element. There are two ways of writing electron configurations: either in terms of the simple Bohr model or in terms of energy sublevels. We now consider how this is done for both methods of writing electron configurations.

EXAM TIP!

Students are often asked in exams to write the electron configuration for a specific element. You could also be asked to determine the number of energy levels, the number of sublevels and the number of orbitals associated with the electron configuration. The following sections will describe in detail how to write the electron configuration and determine the number of energy levels, sublevels and orbitals.

Writing electron configurations – Bohr model

Writing the electron configuration of an element in terms of the Bohr model of the atom may easily be done using the Periodic Table. This method is shown in Example 4.4.

Example 4.4

Question

Write the electronic configuration for potassium showing the number of electrons in each main energy level.

Answers

Step 1

Find potassium in the Periodic Table. Potassium is element number 19, i.e. there are 19 protons in the nucleus and, since all atoms are neutral, there must be 19 electrons in the energy levels around the nucleus in a neutral potassium atom. We must now write down how these electrons are arranged around the nucleus.

Step 2

Go to the beginning of the Periodic Table. Note that in the $n = 1$ period, there are only two elements. This means that the $n = 1$ main energy level can only hold two electrons. Of the nineteen electrons of potassium, **two electrons are in the $n = 1$ main energy level.**

Step 3

Start at the second period and count along from lithium. Note that there are eight elements in the second period, i.e. there are eight electrons in the $n = 2$ main energy level. Thus, we can say that potassium has **eight electrons in the $n = 2$ main energy level.**

Step 4

Start at the third period and count along from sodium. Note that there are eight elements in the third period, i.e. there are eight electrons in the $n = 3$ main energy level. Thus, we can say that potassium has **eight electrons in the $n = 3$ main energy level.**

Step 5

Start at the fourth period. Potassium is the first element you meet, i.e. potassium has **one electron in the $n = 4$ period**.

From the above information, we can write the electronic configuration of potassium as:

K = 2, 8, 8, 1

The electron configurations of the first twenty elements are listed in Table 4.3.

Element	Atomic number	Electrons in each orbit (shell)				Electron configuration
		$n = 1$	$n = 2$	$n = 3$	$n = 4$	
Hydrogen	1	1				1
Helium	2	2				2
Lithium	3	2	1			2,1
Beryllium	4	2	2			2,2
Boron	5	2	3			2,3
Carbon	6	2	4			2,4
Nitrogen	7	2	5			2,5
Oxygen	8	2	6			2,6
Fluorine	9	2	7			2,7
Neon	10	2	8			2,8
Sodium	11	2	8	1		2,8,1
Magnesium	12	2	8	2		2,8,2
Aluminium	13	2	8	3		2,8,3
Silicon	14	2	8	4		2,8,4
Phosphorus	15	2	8	5		2,8,5
Sulfur	16	2	8	6		2,8,6
Chlorine	17	2	8	7		2,8,7
Argon	18	2	8	8		2,8,8
Potassium	19	2	8	8	1	2,8,8,1
Calcium	20	2	8	8	2	2,8,8,2

Table 4.3 The electronic configurations of the first 20 elements given in terms of the simple Bohr picture.

For your exam, you must be able to write the electron configuration of the first 20 elements (and their ions) for Ordinary Level, and of the first 36 elements for Higher Level, in terms of the number of electrons in each main energy level. The electron configuration of transition metal ions is not required. Study Table 4.3 carefully.

- Note that the number of electrons in the outer orbit is the same as the group number in the case of a few groups, e.g. lithium (group I) has one outer electron and beryllium (group II) has two outer electrons.
- In the most recent version of the modern Periodic Table, e.g. the version on p.79 of the Formulae and Tables booklet approved for use in the state exams, this is of limited application as the groups are numbered from 1 to 18.
- In the Periodic Table at the back inside cover of this textbook, both the traditional numbering system of eight groups (I, II, III, etc.) and the new numbering system of 18 groups are included to show the relationship between the two systems.

Study the following examples carefully.

Example 4.5

Question

Write the electronic configuration (s, p) for an atom of oxygen.

Answers

Step 1

Locate the position of oxygen in the Periodic Table. Oxygen is element number 8, i.e. there are eight electrons to be distributed among the sublevels.

Step 2

Starting with hydrogen, we note that there are two electrons in the $n = 1$ main energy level. These two electrons are in the orbital of lowest energy, i.e. the 1s atomic orbital. We indicate that there are two electrons in the 1s sublevel by writing $1s^2$.

Step 3

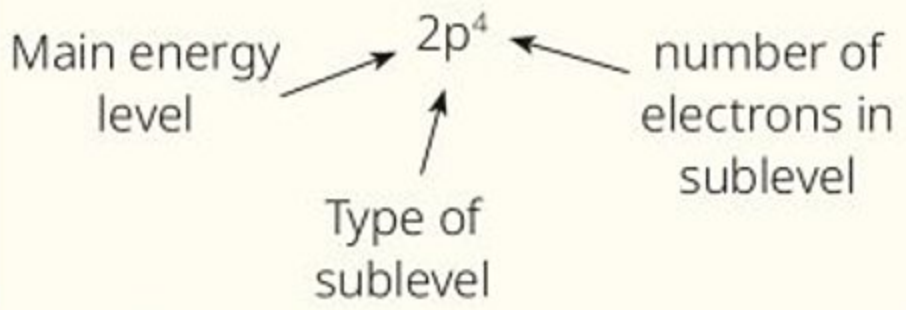
Starting at the second period with lithium, we note that there are two electrons in the 2s orbital ($2s^2$) and four electrons in the 2p orbital ($2p^4$).

Therefore, the electronic configuration of oxygen may be written as:

$O = 1s^2, 2s^2, 2p^4$

Check that the superscripts (2 + 2 + 4) add up to the atomic number of oxygen.

Note carefully the notation that is used in writing electron configurations! The number in front of the letter represents the main energy level, the letter itself represents the type of sublevel and the superscript represents the number of electrons in the sublevel.



Study Example 4.6 in the online resources.

Electron configurations of d-block elements

The electron configurations of the first 36 elements are given in Table 4.5. Note that this table includes the electron configurations of the first row of the d-block elements. For your exam, make sure that you know the names and symbols of the first 36 elements and that you can write the electron configurations of these elements.

H =	$1s^1$
He =	$1s^2$
Li =	$1s^2, 2s^1$
Be =	$1s^2, 2s^2$
B =	$1s^2, 2s^2, 2p^1$
C =	$1s^2, 2s^2, 2p^2$
N =	$1s^2, 2s^2, 2p^3$
O =	$1s^2, 2s^2, 2p^4$
F =	$1s^2, 2s^2, 2p^5$
Ne =	$1s^2, 2s^2, 2p^6$
Na =	$1s^2, 2s^2, 2p^6, 3s^1$
Mg =	$1s^2, 2s^2, 2p^6, 3s^2$
Al =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^1$
Si =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^2$
P =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^3$
S =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^4$
Cl =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^5$
Ar =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6$
K =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$
Ca =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2$
Sc =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^1$
Ti =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^2$
V =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
Cr =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \mathbf{4s^1}, \mathbf{3d^5}$
Mn =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^5$
Fe =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^6$
Co =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^7$
Ni =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^8$
Cu =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, \mathbf{4s^1}, \mathbf{3d^{10}}$
Zn =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$
Ga =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^1$
Ge =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^2$
As =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^3$
Se =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^4$
Br =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^5$
Kr =	$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}, 4p^6$

Table 4.5 The electron configurations of the first 36 elements.

Writing electron configurations: Determining the number of energy sublevels and orbitals

We will now consider how to write the electron configurations of the elements in terms of sublevels.

As stated in the previous chapter, the following information was deduced by scientists from their study of spectra:

- Each main energy level, excluding the first, consists of a number of sublevels. The $n = 2$ main energy level has two sublevels, the $n = 3$ main energy level has three sublevels and the $n = 4$ main energy level has four sublevels. These sublevels are shown in Figure 4.11.

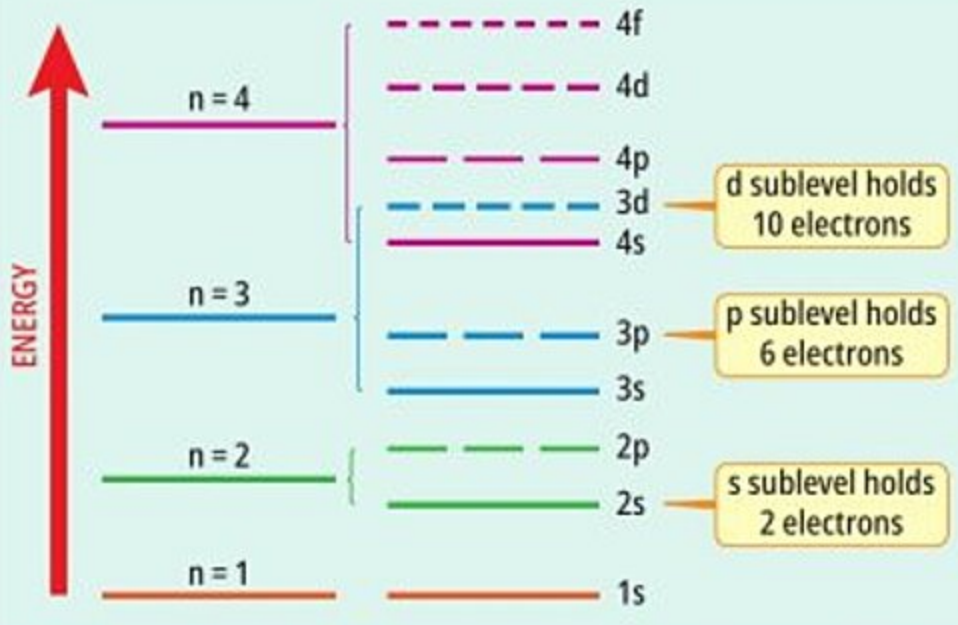


Figure 4.11 All of the main energy levels except the first consist of sublevels. An s sublevel contains one s atomic orbital, a p sublevel contains three p atomic orbitals, and a d sublevel contains five d atomic orbitals. The maximum number of electrons that can be accommodated in an orbital is 2.

Note in Figure 4.11 that an s sublevel contains one s atomic orbital, a p sublevel contains three p atomic orbitals and a d sublevel contains five d atomic orbitals.

- An **s sublevel can hold two electrons,** i.e. a single s orbital can hold two electrons. It has also been discovered that a **p sublevel can hold six electrons**, i.e. two electrons in each of the three p orbitals, p_x, p_y and p_z.
- It was also found that a **d sublevel can hold ten electrons**, i.e. two electrons in each of the five d orbitals. (In this course, you are not required to know anything about the f sublevel.)

The above ideas are summarised in Table 4.4.

Type of sublevel	Number of orbitals in sublevel	Maximum number of electrons in sublevel
s	1	2
p	3	6
d	5	10

Table 4.4 This table summarises the number of orbitals and maximum number of electrons in each type of sublevel.

Note that a p sublevel consists of three p orbitals of equal energy. Since each p orbital can contain two electrons, then a p sublevel can contain 6 electrons.

A d sublevel consists of five d orbitals of equal energy. Since each d orbital can contain two electrons, then a d sublevel can contain 10 electrons.

There is a very simple rule for assigning electrons to the various sublevels.

Aufbau Principle: When building up the electron configuration of an atom in its ground state, the electrons occupy the lowest available energy levels.

If you study Figure 4.11 you will see that the order in which the sublevels are filled is 1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, etc. There is no need to learn off this order as it may easily be deduced from the Periodic Table:

- The Periodic Table may be divided into four blocks: s block, p block, d block and f block.
- All the elements in the s block have their outer electrons in an s sublevel.
- All the elements in the p block have their outer electrons in a p sublevel.
- All the elements in the d block have their outer electrons in a d sublevel, Figure 4.12

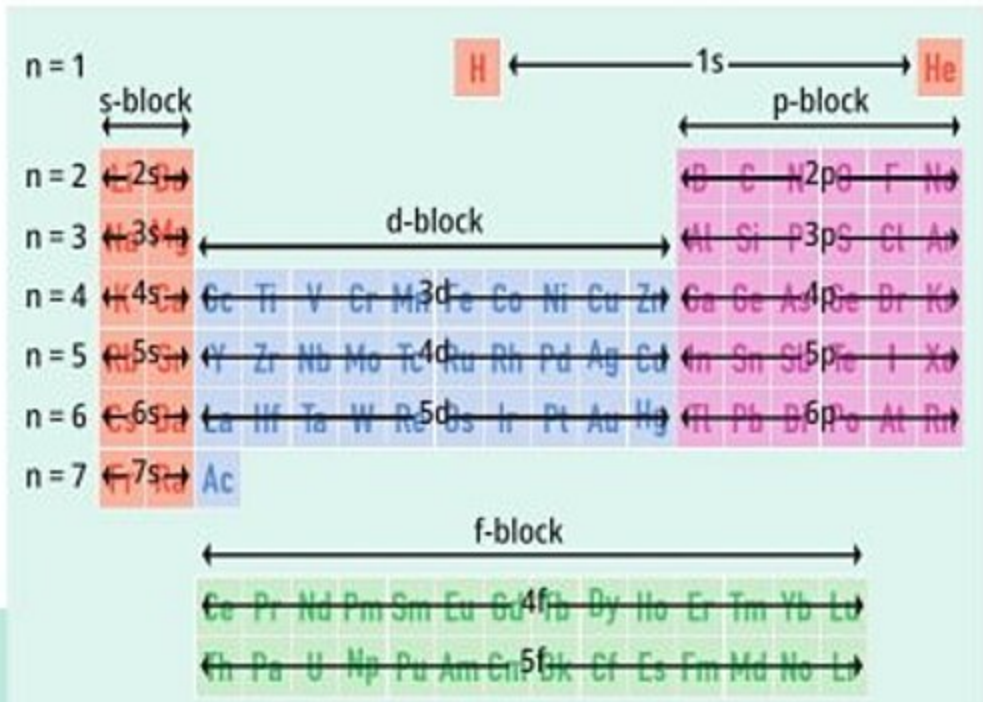


Figure 4.12 The electron configurations (s, p, d, f) may easily be deduced from the Periodic Table.

Note the following points when writing electron configurations:

- Since the 4s sublevel is lower in energy than the 3d sublevel, **the 4s sublevel is always filled before the 3d sublevel.** Using the Periodic Table will help you to write down the electron configurations of the d-block elements. Simply write down the electron configuration of calcium as shown in Example 4.6, count along the first row of the d-block (scandium, titanium, vanadium, etc.) and put the required number of electrons into the 3d sublevel. For example, since iron is the sixth element along the row, we put six electrons into the 3d sublevel, i.e. the electron configuration of iron is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, **$4s^2$**, **$3d^6$**.
- Note that there are ten elements in the first row of the d-block elements. This is because the d sublevel can hold ten electrons. Therefore, the $n = 3$ main energy level can hold a total of eighteen electrons: two electrons in the 3s sublevel, six electrons in the 3p sublevel, and ten electrons in the 3d sublevel.
- The number of electrons that any main energy level can hold may be calculated from the formula $2n^2$. Thus, the $n = 1$ main energy level can hold two electrons, the $n = 2$ main energy level can hold eight electrons, and the $n = 3$ main energy level can hold eighteen electrons.
- If you study Table 4.5 you will see that the electron configurations of chromium and copper are not what you might expect. You might think that the electron configuration of chromium would be:
  - Cr = $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^4$ rather than Cr = $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^5$ as written in Table 4.5. However, it has been found that **sublevels that are exactly half filled or completely filled have extra stability**. Therefore, one of the electrons in the $4s^2$ orbital 'flips over' into one of the d orbitals to give two sublevels which are exactly half filled. Therefore, the electron configuration of chromium is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, **$4s^1$**, **$3d^5$**.
- The situation with copper is rather similar to that of chromium. You might expect the electron configuration of copper to be :
  - Cu = $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^9$ rather than Cu = $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^{10}$ as shown in Table 4.5. However, scientists explained this stability by stating that one of the electrons in the $4s^2$ orbital 'flips over' to one of the d orbitals. The completely filled 3d sublevel and the half-filled 4s sublevel have extra stability associated with them. Hence the electron configuration of copper is $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, **$4s^1$**, **$3d^{10}$**.

For your exam, you are expected to know how to write the electron configurations of the first 36 elements and their ions (excluding transition metal ions) in terms of their s, p, d configurations. Therefore, Table 4.5 should be studied carefully! Also, if you are asked to write the electron configuration of either copper or chromium, alarm bells should start ringing in your head!

4.8 Writing electron configurations of ions

An atom that has lost or gained electrons is called an ion. Since electrons are negatively charged, an atom that gains electrons becomes negatively charged. On the other hand, an atom that loses electrons becomes positively charged. We make use of these facts when writing the electron configuration of an ion.

Example 4.7

Question

Write the electronic configuration (s, p) of the Al^{3+} ion. What neutral atom has the same configuration?

Answer

Step 1

Locate the position of aluminium in the Periodic Table. Aluminium is element number 13, i.e. an atom of aluminium has 13 electrons.

Step 2

Work out the number of electrons in the ion. Since the aluminium ion has three positive charges, it must have lost three electrons. Thus, the Al^{3+} ion has 10 electrons, i.e. the same number of electrons as an atom of neon. Therefore, the electronic configuration of the Al^{3+} ion will be the same as an atom of neon.

$Al^{3+} = 1s^2, 2s^2, 2p^6$

» Study Example 4.8 in the online resources.

» Study Example 4.9 in the online resources.

4.9 Arrangement of electrons in orbitals of equal energy

In writing electron configurations, we have not yet considered how electrons are distributed in individual orbitals of equal energy. For example, we have written the electron configuration of nitrogen as $1s^2, 2s^2, 2p^3$. We now ask ourselves the question: How are the three electrons in the p sublevel distributed among the three p orbitals?

In 1927 Friedrich Hund, having studied the spectra of various elements, put forward an important rule in answer to this question. This rule is called Hund's Rule of Maximum Multiplicity.

Hund's Rule of Maximum Multiplicity states that when two or more orbitals of equal energy are available, the electrons occupy them singly before filling them in pairs.

If we apply this rule to the nitrogen atom, it simply means that of the three electrons added to the 2p sublevel, one electron will enter the p_x orbital, the second will enter the p_y and the third will enter the p_z. Thus, there is the maximum number of unpaired electrons, Figure 4.13.

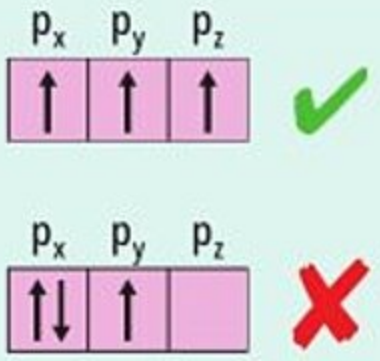


Figure 4.13 The three p electrons of nitrogen occupy the p orbitals singly to give the maximum number of unpaired electrons (Hund's Rule).

These 'electrons-in-boxes' diagrams are used to show how electrons are distributed in orbitals. The box represents the orbital and the arrow represents the electron. Arrows are used because it was discovered that as electrons revolve around the nucleus, they spin on their own axes. (This is rather like the Earth spinning on its axis as it revolves around the Sun). However, the electrons can spin in either a clockwise direction or an anti-clockwise direction.

In 1925 Wolfgang Pauli, from his study of spectra, made a very important deduction called the **Pauli Exclusion Principle**.

The **Pauli Exclusion Principle** states that no more than two electrons may occupy an orbital and they must have opposite spin.

The arrows are used to indicate the direction of spin of the electrons. The ↓ represents an electron spinning clockwise and ↑ represents an electron spinning anti-clockwise. The 'electrons-in-boxes' method of representing the electron arrangements in atoms is shown for the atoms of the first ten elements in Figure 4.14.

The distribution of electrons among the p orbitals may also be shown using a more detailed form of the electron configurations given in Table 4.5. For example, the electron configurations of the elements from boron to neon may also be written as:

$B = 1s^2, 2s^2, 2p_x^1, 2p_y^0, 2p_z^0$

$C = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^0$

$N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

$O = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

$F = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$

$Ne = 1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$

The 'electrons-in-boxes' diagrams or the extended forms of electron configurations as written above need only be given if you are specifically asked about the distribution of electrons in the p sublevel (see Example 4.11). In all other cases, the electron configurations as given in Table 4.5 are perfectly adequate.

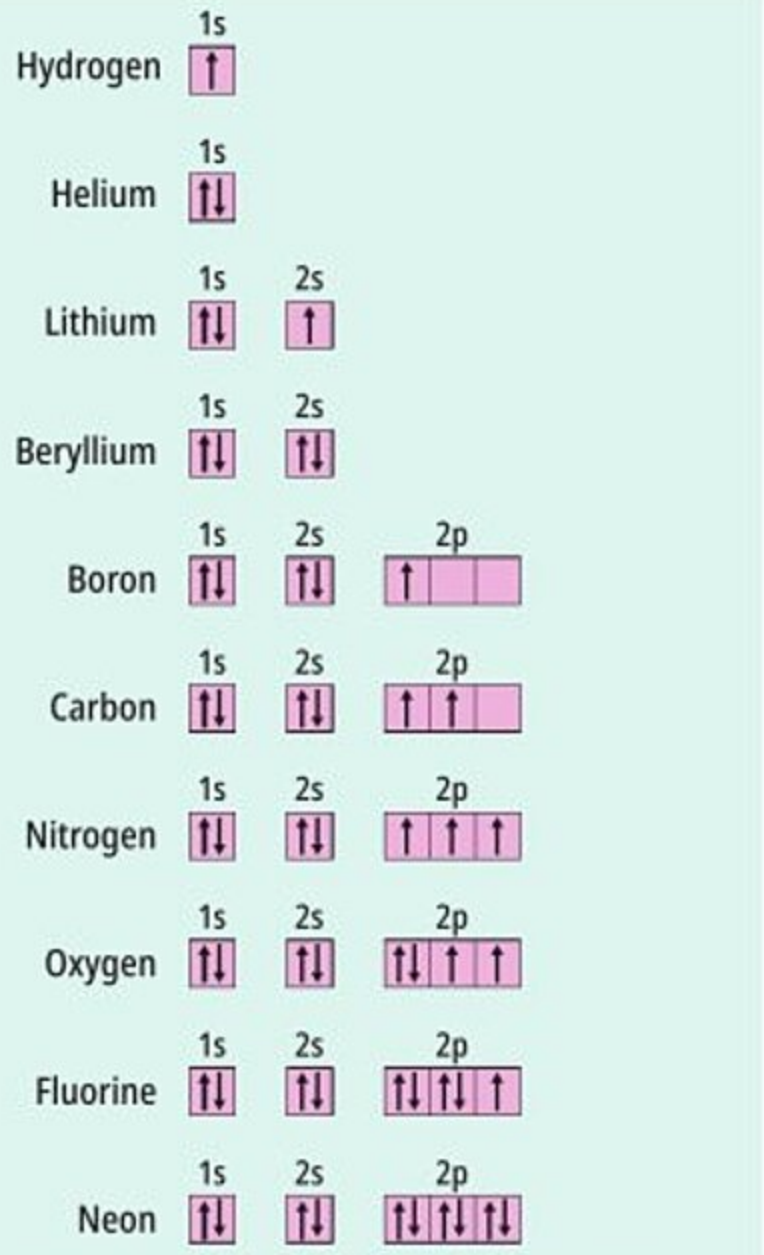


Figure 4.14 The 'electrons-in-boxes' method of representing the electron configurations of the first ten elements.

Example 4.10

Question

Write the s, p electron configuration for the potassium atom.

Hence state how many (i) energy sublevels, (ii) individual orbitals are occupied by electrons in a potassium atom. [LCH]

Answer

$K = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

(i) There are 6 energy sublevels occupied in a potassium atom, i.e. 1s, 2s, 2p, 3s, 3p and 4s.

(ii) There are 10 individual orbitals occupied in a potassium atom, i.e. 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, $3p_z$ and 4s.

Example 4.11

Question

Write the electron configuration (s, p) for the sulfur atom in its ground state, showing the arrangement in atomic orbitals of the highest energy electrons.

State how many (i) energy levels, (ii) orbitals are occupied in a sulfur atom in its ground state. [LCH]

Answer

Sulfur = $1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^1, 3p_z^1$.

(i) There are 3 energy levels occupied in a sulfur atom in its ground state, i.e. $n = 1$, $n = 2$ and $n = 3$.

(ii) There are 9 orbitals occupied in a sulfur atom in its ground state, i.e. 1s, 2s, $2p_x$, $2p_y$, $2p_z$, 3s, $3p_x$, $3p_y$, $3p_z$.

TEST YOURSELF: Attempt Questions 4.3–4.4 and W4.4–W4.12.

Summary What I should know

- An element is defined as a substance that cannot be split into simpler substances by chemical means.
- Mendeleev's Periodic Law states that when elements are arranged in order of increasing atomic weight (relative atomic mass), the properties of elements with similar properties repeat at regular intervals.
- Henry Moseley used X-rays to determine the atomic number of an element, i.e. the number of protons in the nucleus of an atom.
- The modern Periodic Table is an arrangement of elements in order of increasing atomic number.
- The mass number of an element is the sum of the number of protons and neutrons in the nucleus of an atom of that element.
- Isotopes are atoms of the same element (i.e. they have the same atomic number) which have different mass numbers due to the different number of neutrons in their nuclei.
- Relative atomic mass (atomic weight) is defined as the average of the mass numbers of the isotopes of the element, as they occur naturally, taking their abundances into account and expressed on a scale in which the atoms of the carbon-12 isotope have a mass of exactly 12 units.
- The electron configuration of an element shows the arrangement of electrons in an atom of that element.
- The Aufbau Principle states that when building up the electron configuration of an atom in its ground state, the electrons occupy the lowest available energy level.
- Hund's Rule of Maximum Multiplicity states that when two or more orbitals of equal energy are available, the electrons occupy them singly before filling them in pairs.
- The Pauli Exclusion Principle states that no more than two electrons may occupy an orbital and they must have opposite spin.

Learning outcomes

At the end of this chapter, I should be able to:			
Describe the development of the modern Periodic Table including the significance of the contribution of Mendeleev.	⬡	⬡	⬡
Compare Mendeleev's Periodic Table with the modern Periodic Table.	⬡	⬡	⬡
Explain the meaning of the terms *atomic number*, *mass number*, *relative atomic mass* and *isotopes*.	⬡	⬡	⬡
Describe how to write electron configurations of elements and ions.	⬡	⬡	⬡

Chapter review questions

4.1 **(a)** Name the Irish chemist who was the first scientist to give a proper definition of the term *element*.

(b) Who discovered sodium, potassium and a number of other elements?

(c) Name the scientist who developed a method of determining the atomic number of an element.

(d) State the Periodic Law.

(e) Define relative atomic mass.

(f) How many (i) neutrons, (ii) electrons are there in the ion $^{17}_{10}Cl^{-}$?

(g) Iridium has two naturally occurring stable isotopes, iridium–191 and iridium–193. What are isotopes? [LCH]

(h) (i) Name the instrument used to identify isotopes of elements

(ii) Calculate the approximate relative atomic mass of gallium given that it contains 60% of the isotope $^{69}_{31}Ga$ and 40% of the isotope $^{71}_{31}Ga$.

(i) Why did Mendeleev place tellurium before iodine in his periodic table of the elements? [LCH]

4.2 To celebrate the 150th anniversary of the discovery of the periodic system, 2019 has been designated as the International Year of the Periodic Table of Chemical Elements by the United Nations (UN), Figure 4.15.

(a) (i) What is meant by the *periodic system* in the context of Mendeleev's 1869 periodic table of the elements?

(ii) Comment on the positioning of tellurium (**Te**) and iodine (**I**) in the 1869 table.

(iii) Why did the 1869 table not include any noble gases?

(b) Modern periodic tables arrange the elements in order of <u>atomic number</u> and not in order of relative atomic mass.

(i) Define the underlined term.

(ii) Give an advantage of arranging the elements in order of atomic number. [LCH]

4.3 **(a)** Write the electron configuration for (i) the fluorine atom, (ii) the calcium ion.

(b) Write down the s, p, d configuration for (i) chromium, (ii) manganese.

(c) What do the ions O^{2-}, F^{-}, Na^{+} and Mg^{2+} have in common?

(d) What atoms are represented by the following structures: (i) $1s^2, 2s^2, 2p^3$ (ii) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^{10}$?

(e) The electron configuration for a metal ion M^{3+} is $1s^2, 2s^2, 2p^6$. Write the s, p configuration for the metal atom.

(f) Show, using a diagram or otherwise, how the electrons in an atom of fluorine are distributed among the p orbitals .

4.4 The electronic arrangement of the boron atom in its ground state can be shown as follows (where each arrow signifies an electron).

1s	2s	$2P_x$	$2P_y$	$2P_z$
↑↓	↑↓	↓		

Show in a similar manner the ground state electronic arrangement of an atom of (i) carbon, (ii) nitrogen, (iii) oxygen.

Name and state the rule illustrated by the electron configurations you have shown.

Write the s, p, d ground state configuration of the atom with atomic number 21, putting the sublevels in the order in which they are filled.

[LCH]

Figure 4.15

5 Chemical Bonding and Structure

OBJECTIVES

- To give students an understanding of some of the main types of chemical bonding.
- To ensure that students know how to write the chemical formulas of compounds.
- To enable students to predict the shapes of molecules.
- To provide students with the opportunity to test for the presence of anions (negative ions) in solutions of their salts.

5.1 Introduction

Most of the materials around us are made from combinations of elements. For example, water is formed when hydrogen and oxygen combine together; table salt is formed by combining sodium and chlorine; carbon dioxide is formed when carbon and oxygen combine together. Substances made by joining together two or more different elements are called **compounds**.

A **compound** is a substance that is made up of two or more different elements combined together chemically.

When elements combine to form compounds, there are attractive forces that hold the atoms together in this new compound. These attractive forces are called **chemical bonds**. In this chapter, we will study the different types of chemical bonds that exist. We will see how a knowledge of chemical bonding helps us to understand chemical formulas, e.g. why the formula for water is H_2O and not H_3O. We will learn how to write chemical formulas and how to name compounds.

It will become quite easy for us to understand chemical bonding if we first study an important rule called the Octet Rule.

5.2 The Octet Rule

Chemists have observed that the noble gases (e.g. helium, neon, argon) in Group 18 or VIII of the Periodic Table are very unreactive, i.e. they form practically no compounds. Hence, they are often called the 'inert' gases (noble gases), Figure 5.1.

All the noble gases consist of single atoms. This is explained by saying that these elements do not react because they have stable electron configurations. Since all the noble gases (except helium) have eight electrons in their outer energy level, the rule was called the octet rule (octet = eight).

Figure 5.1 Helium and argon are two of the noble (inert) gases. Helium is a very light gas and is safe for use in filling balloons as it is so unreactive. Argon is used in medical lasers to perform surgery.

Octet Rule: When bonding occurs, atoms tend to reach an electron arrangement with eight electrons in the outermost energy level.

Therefore, when elements react together to form compounds, their atoms tend to change their electron arrangement so that they end up with eight electrons in their outermost energy level. It is important to realise that the octet rule is more a 'rule of thumb' rather than a strict chemical law.

There are limitations in predicting bonding between atoms and one of these limitations is that there are a number of exceptions to the octet rule:

- **Transition metals do not usually obey the octet rule.** In many of their compounds, transition metals can have more or fewer than eight electrons in their outermost energy level.
- **Helium is unreactive, as it contains a full outer energy level of two electrons**. In addition, the elements near helium in the Periodic Table (hydrogen, lithium and beryllium) tend to achieve the same electron arrangement as helium, with two electrons in the outer energy level rather than the eight electrons of the other noble gases.

We will now study how the octet rule helps us to understand the two main types of chemical bonds: **ionic bonds** and **covalent bonds**.

5.3 Ionic bonding: Transfer of electrons

Atoms can obtain the electron configuration of a noble gas by gaining or losing electrons. When an atom gains or loses electrons, it becomes a charged atom. A charged atom is called an ion. As we shall see later, a group of atoms carrying a charge is also called an ion.

An **ion** is a charged atom or group of atoms.

- The elements in Group I of the Periodic Table tend to lose one electron to form an ion with one positive charge.
- The elements in Group II of the Periodic Table tend to lose two electrons to form an ion with two positive charges.
- In an atom that has lost electrons, there are more protons in the nucleus than there are electrons in orbit around it. Therefore, the ion formed is positively charged.
- A **positive ion** is called a **cation**. The formation of some positive ions may be shown simply as follows:

$$Na \longrightarrow Na^{+} + e^{-} \qquad Ca \longrightarrow Ca^{2+} + 2e^{-}$$
$$2,8,1 \qquad 2,8 \qquad\qquad 2,8,8,2 \qquad 2,8,8$$

- The elements in Groups VII (or 17) tend to gain one electron and the elements in Group VI (or 16) of the Periodic Table tend to gain two electrons to form **negative ions**. Negative ions are called **anions**.

$$Cl + e^{-} \longrightarrow Cl^{-} \qquad O + 2e^{-} \longrightarrow O^{2-}$$
$$2,8,7 \qquad 2,8,8 \qquad\qquad 2,6 \qquad 2,8$$

Note that in each case, the ion formed has the electron configuration of the noble gas that is nearest to it in the Periodic Table. It is the formation of this stable electron configuration that is the 'driving force' behind the formation of the ion. Once ions are formed, they are held together in a compound by the force of attraction that exists between oppositely charged ions. This force of attraction is called an ionic bond.

An **ionic bond** is the force of attraction between oppositely charged ions in a compound. Ionic bonds are always formed by the complete transfer of electrons from one atom to another.

Common table salt (sodium chloride) is one of the best-known examples of an ionic substance, i.e. a substance held together by ionic bonding.

Using Lewis diagrams to show the formation of ionic bonding

There are two ways of showing the formation of the ionic bonding in sodium chloride: either in terms of the Bohr-type circle diagram, Figure 5.2(a), or in terms of Lewis diagrams, Figure 5.2(b). These diagrams are so called because it was Gilbert Lewis, an American chemist, Figure 5.3 who invented this system to describe chemical bonding. Lewis diagrams are also called Lewis formulas or Lewis dot-and-cross structures.

Note the following points:

- In drawing Lewis electron dot-and-cross diagrams, the outer electrons of one atom are represented by dots, with crosses used for the electrons of the other atom. The numbers under the chemical symbols show the arrangement of electrons in the energy levels.
- The transfer of electrons is shown by the arrow in the Lewis dot-and-cross diagrams.
- Unless otherwise requested, both methods of representing ionic bond formation are equally acceptable in an exam, provided the electron configuration is written as shown in Figure 5.2.
- Bohr-type circle diagrams can be time-consuming to draw and they give more information than we need, since it is only the electrons in the outermost orbit, known as **valence electrons**, that are involved in bonding. Therefore, we will use Lewis dot-and-cross diagrams as much as possible in this textbook.

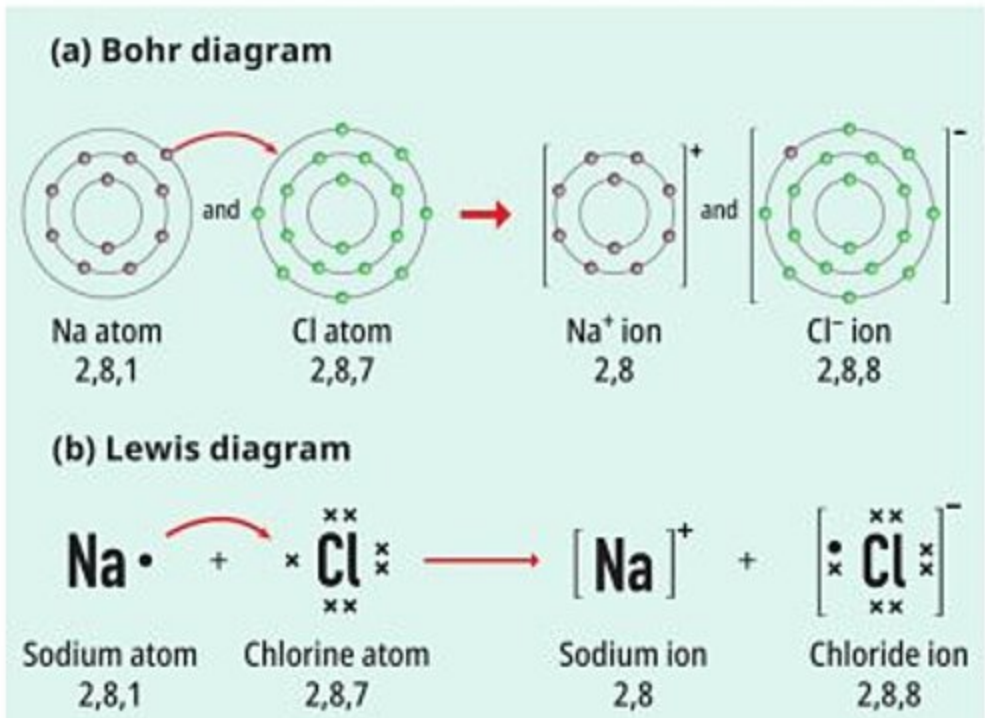


Figure 5.2 (a) The formation of the ionic bond in sodium chloride using the Bohr-type diagram. (b) The formation of the ionic bond in sodium chloride using Lewis diagrams.

Figure 5.3

Gilbert Lewis
(1875–1946)

Gilbert Lewis was an American chemist who introduced a simple way to represent valence (outermost) electrons using dots and crosses around symbols of elements. These help to give us a picture of how atoms and ions are bonded together. He loved teaching and was a great chemistry teacher, as evidenced by the simple dot-and-cross system that he developed to explain bonding.

Example 5.1

Question

Show the formation of the ionic bonds in magnesium fluoride, MgF_2, by means of a suitable diagram.

Answer

Each magnesium atom loses two electron, while each fluorine atom gains only one electron. Therefore, there must be two fluorine atoms for every one magnesium atom (Figure 5.4).

Figure 5.4 The formation of the ionic bond in magnesium fluoride, MgF_2.

Sodium chloride crystal structure

X-ray studies enable chemists to work out the arrangement of ions in a crystal. Sodium chloride, for example, has a cubic structure, Figure 5.5.

Note the following points about the structure of sodium chloride:

- Although Figure 5.5 shows only 27 ions, remember that the structure of sodium chloride consists of a regular three-dimensional arrangement of millions of sodium ions and chloride ions.
- The three-dimensional arrangement of ions is called a **crystal lattice**.
- In Figure 5.5 we see the repeating unit in the crystal lattice. This repeating unit is called the **unit cell** of sodium chloride and it repeats itself in all directions to build up the crystal.
- In the crystal lattice, each sodium ion is surrounded by six chloride ions and each chloride ion is surrounded by six sodium ions. In fact, ions are so small that the tiniest crystal of sodium chloride consists of millions of ions!

Figure 5.5 This diagram represents the crystal structure of sodium chloride, i.e. how the ions are packed together in the crystal.

Salt is used as a food preservative and in the chemical industry to manufacture soap, sodium metal, chlorine gas, detergents, toothpaste and washing soda. Also, it is spread on roads during the winter to help melt frost and snow.

5.4 How to write the formulas of ionic compounds

A **chemical formula** is a way of representing a compound using symbols for the atoms present and numbers to show how many atoms of each element are present. We have seen in Example 5.1 that the chemical formula for magnesium fluoride is MgF_2. This tells us that the compound magnesium fluoride consists of magnesium and fluorine. It also tells us that there are twice as many fluoride ions as magnesium ions in a crystal of magnesium fluoride.

The following are the key points for writing the formulas of ionic compounds:

- Ionic compounds are formed between the elements of Groups 1 and 2 (**metals**) and those of Groups VI (or 16) and VII (or 17) (**non-metals**) of the Periodic Table. In general, ionic compounds are usually formed when metals react with non-metals. (The 'steps of stairs' on the Periodic Table going from boron to astatine divide the metals on the left from the non-metals on the right.)
- Metals have a tendency to lose electrons, and non-metals have a tendency to gain electrons. The number of electrons lost or gained depends on the group in which the elements are located.
- An ionic compound is neutral overall. Therefore, there must be the same number of positive charges as negative charges present in the compound.

Some ions of the first 36 elements (excluding the d-block metals) are shown in Figure 5.6. Studying the following examples will help you to understand how to write the formulas of ionic compounds.

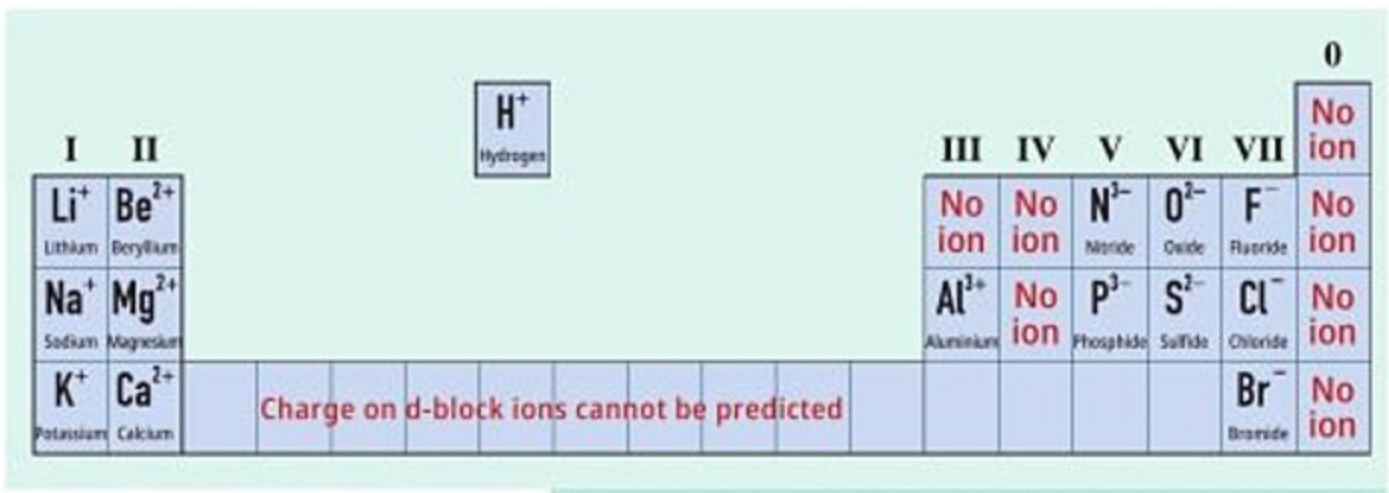


Figure 5.6 Some ions of the first 36 elements

Example 5.2

Question

Write the formula of potassium bromide.

Answer

The potassium ion is K^+. The bromide ion is Br^-. The formula K^+Br^- is correct, since there is the same number of positive and negative charges.

Answer: The formula of potassium bromide is KBr.

Example 5.3

Question

Write the formula of calcium chloride.

Answer

The calcium ion is Ca^{2+}. The chloride ion is Cl^-. The formula $Ca^{2+}Cl^-$ is not correct, since there are two positive charges but only one negative charge. To get two negative charges, we must have two Cl^- ions.

Answer: The formula of calcium chloride is $CaCl_2$.

Example 5.4

Question

Write the formula of sodium sulfide.

Answer

The sodium ion is Na^+. The sulfide ion is S^{2-}. The formula Na^+S^{2-} is not correct, since there is one positive charge but two negative charges. To get two positive charges, we must have two Na^+ ions.

Answer: The formula of sodium sulfide is Na_2S.

Example 5.5

Question

Write the formula of aluminium oxide.

Answer

The aluminium ion is Al^{3+}. The oxide ion is O^{2-}. The formula $Al^{3+}O^{2-}$ is not correct, since there are three positive charges but only two negative charges. Bring all charges up to their lowest common denominator, i.e. 6. To get six positive charges, we need two aluminium ions. To get six negative charges, we need three oxide ions, i.e. $(Al^{3+})_2\ (O^{2-})_3$

Answer: The formula of aluminium oxide is Al_2O_3.

Writing formulas of compounds with group ions

As mentioned earlier, an ion can be a charged atom or a group of atoms. There are many ionic compounds that contain group ions, e.g. the sulfate ion, the carbonate ion and the nitrate ion. For example, barium sulfate is used in X-ray examinations of internal organs, chalk is calcium carbonate and sodium hydrogencarbonate (bread soda) is used in baking.

The group ions commonly encountered in this course are listed in Table 5.1. It is not possible to predict the formulas of group ions from the Periodic Table, so learn them off by heart!

Name	Formula	
Hydroxide ion	OH^-	One negative charge
Nitrate ion	NO_3^-	
Hydrogencarbonate ion	HCO_3^-	
Permanganate ion	MnO_4^-	
Carbonate ion	CO_3^{2-}	Two negative charges
Chromate ion	CrO_4^{2-}	
Dichromate ion	$Cr_2O_7^{2-}$	
Sulfate ion	SO_4^{2-}	
Sulfite ion	SO_3^{2-}	
Thiosulfate ion	$S_2O_3^{2-}$	
Phosphate ion	PO_4^{3-}	Three negative charges
Ammonium ion	NH_4^+	One positive charge

Table 5.1 Some common group ions

The following examples will help you to write the formulas of ionic compounds that have group ions.

Example 5.6

Question

Write the formula of potassium hydroxide.

Answer

The potassium ion is K^+. The hydroxide ion is OH^-. The formula K^+OH^- is correct, since there is the same number of positive and negative charges.

Answer: The formula of potassium hydroxide is KOH.

Example 5.7

Question

Write the formula of sodium sulfate.

Answer

The sodium ion is Na^+. The sulfate ion is SO_4^{2-}. The formula $Na^+SO_4^{2-}$ is not correct, since there is one positive charge but two negative charges. To get two positive charges, we must have two Na^+ ions.

Answer: The formula of sodium sulfate is Na_2SO_4.

Writing formulas of compounds containing transition metals

You will see in Figure 5.6 (p.53) that we have indicated that it is not possible to predict the charges of the ions of the transition metals. In this course, we will meet a number of transition metal compounds.

Transition metals often have **variable valency**, Figure 5.7. The word 'valency' means 'combining power'. (A more formal definition of valency will be given in Section 5.6.)

Transition metals exhibit variable valency because there is such a small energy difference between the 4s and 3d sublevels. This means that the transition metals can lose different numbers of electrons from these sublevels to give metal ions with different positive charges.

The following are the main transition metals that show variable valency and their compounds that we will meet in this course:

Iron	Iron combines with chlorine to form either $FeCl_2$ or $FeCl_3$. The compound $FeCl_2$ is an ionic compound and the +2 charge on the iron atom is represented by putting the Roman numeral II in brackets. Therefore, $FeCl_2$ is called iron(II) chloride. Similarly, the compound $FeCl_3$ is called iron(III) chloride.
Copper	Copper combines with oxygen to form either Cu_2O or CuO. Cu_2O is called copper(I) oxide and CuO is called copper(II) oxide.
Chromium	Chromium exists as Cr^{3+} ions in chromium(III) chloride, $CrCl_3$. In $Na_2Cr_2O_7$, sodium dichromate, it appears that there are Cr^{6+} ions. (We shall clarify this in Chapter 14.) Hence sodium dichromate is also written sodium dichromate(VI).
Manganese	Manganese also shows variable valency. MnO_2 is an ionic compound called manganese(IV) oxide – commonly called manganese dioxide. $MnSO_4$ is called manganese(II) sulfate and $KMnO_4$, is commonly called potassium permanganate – it is also called potassium manganate(VII).

Figure 5.7 All these solutions contain transition metal ions. All these ions have variable valency. Note also that when dissolved in water, they all form coloured solutions.

Example 5.8

Question

Write the formula of calcium hydrogencarbonate.

Answer

The calcium ion is Ca^{2+}. The hydrogencarbonate ion is HCO_3^-. The formula $Ca^{2+}HCO_3^-$ is not correct, since there are two positive charges but only one negative charge. To get two negative charges, we must have two HCO_3^- ions, i.e. $Ca^{2+}(HCO_3^-)_2$

Answer: The formula of calcium hydrogencarbonate is $Ca(HCO_3)_2$.

Example 5.9

Question

Write the formula of iron(II) carbonate.

Answer

The Roman number (II) indicates Fe^{2+}. The carbonate ion is CO_3^{2-}. The formula $Fe^{2+}CO_3^{2-}$ is correct, since there are two positive charges and two negative charges.

Answer: The formula of iron(II) carbonate is $FeCO_3$.

Example 5.10

Question

Name the compound $Cr_2(SO_4)_3$.

Answer

The three sulfate ions together give a total negative charge of –6. Since the overall charge must be zero, the two chromium atoms must carry a total charge of +6. Therefore, each Cr atom must be Cr^{3+}. Therefore, the name of the compound is chromium(III) sulfate.

Answer: Chromium(III) sulfate.

NOTE

Do not get confused between compounds whose names end in **-ide** and those whose names end in **-ate**. A compound that contains just two elements always ends in -ide, e.g. magnesium sulfide, MgS. (Hydroxides are an exception to this rule.) Compounds whose names end in **-ate** contain oxygen as well as the other two elements, e.g. magnesium sulfate, $MgSO_4$.

5.5 d-Block elements and transition elements

In many cases, there is no distinction made between the d-block elements and the transition elements. When referring to the s, p, d and f blocks of the Periodic Table, transition elements are regarded as those in the d-block of the table. However, if one examines the first row of the d-block from scandium to zinc, it is found that the properties of scandium and zinc are quite different from those of the other eight elements in this row. All the elements from titanium to copper inclusive are referred to as transition elements or transition metals. These show certain characteristics:

- **Transition metals have variable valency.** However, scandium only forms Sc^{3+} ions and zinc only forms Zn^{2+} ions.
- **Transition metals usually form coloured compounds.** However, scandium and zinc only form white compounds.
- **Transition metals are widely used as catalysts (Chapter 17).** However, scandium and zinc show little catalytic activity.

Since scandium and zinc do not have typical transition metal properties, chemists devised a definition of transition metals that excludes these two elements but includes the elements from titanium to copper.

A **transition metal** is one that forms at least one ion with a partially filled d sublevel.

Neither Sc^{3+} nor Zn^{2+} has a **partially** filled d sublevel.

$Sc^{3+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

$Zn^{2+} = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^{10}$

In the case of Sc^{3+} the d sublevel is completely empty. In the case of Zn^{2+} the d sublevel is completely full. Since the properties of transition metals are associated with partly filled d sublevels, scandium and zinc are not considered transition metals.

In short, **all of the ten elements from scandium to zinc are d-block elements but only those eight elements from titanium to copper (inclusive) are transition metals**.

TEST YOURSELF: Attempt Questions 5.1 and W5.1–W 5.2.

5.6 Covalent bonding: Sharing of electrons

When studying ionic bonding, you learned that ionic compounds are usually formed when metals react with non-metals. However, there are many compounds that contain only non-metals, e.g. water, ammonia and carbon dioxide. These compounds do not contain any ions. Instead, the atoms achieve noble gas configurations by **sharing** electrons. A bond formed by sharing of electrons is called a covalent bond.

A **covalent bond** is a chemical bond that is formed when two atoms share one or more pairs of electrons.

The word 'covalent' comes from the prefix 'co' meaning 'shared' and the Latin word *valent* meaning 'ability', i.e. the ability of an atom to combine with other atoms.

Covalent bonding results in the formation of a molecule.

A **molecule** is a group of atoms joined together. It is the smallest particle of an element or compound that can exist independently.

A molecule of hydrogen gas is written as H_2 and a molecule of water is written as H_2O.

Do not get confused between the terms *molecule* and *compound*. A compound consists of two or more different elements chemically combined, e.g. H_2O is a compound as it contains two different elements. H_2O also represents a molecule as it contains a group of atoms joined together. H_2 represents a molecule of hydrogen. However, it is not a compound, as both atoms are of the same element.

Note: Noble gases such as helium (He), neon (Ne) and argon (Ar), naturally exist as single atoms. They are said to be monatomic (one atom). Therefore, a molecule for a monoatomic element refers to the single atom that represents the smallest particle of the element that can exist independently.

To help you understand this idea of electrons being shared, we now consider a number of examples. It is difficult to show the shapes of molecules on paper, as most molecules are three-dimensional. Therefore, for each example, you will see a photograph of a model of each molecule made using a *Molymod* kit. It is recommended that you make these molecules yourselves and play with them to help you understand the shape!

Note: As with ionic bonding, covalent bonding also involves only the outer electrons. The shared pairs of electrons in a covalent bond are often represented simply by a dash.

The term *molecule* can only be used for covalent compounds. Since ionic compounds consist of giant structures of ions, it is not correct to refer to a 'molecule' of sodium chloride.

Example 5.11

The Hydrogen Molecule, H_2

- A hydrogen atom has just one electron in its outer (and only) energy level.
- It is found that two hydrogen atoms join together to form a hydrogen molecule, H_2. A cylinder of hydrogen gas consists of millions of these tiny independent units, each of which is called a **molecule** of hydrogen.
- A hydrogen molecule is formed when one hydrogen atom shares its single electron with another hydrogen atom.
- The second hydrogen atom shares its single electron with the first hydrogen atom.
- Two electrons are therefore shared between the two hydrogen atoms. It can be said that each hydrogen atom has a share of two electrons in its outermost energy level or orbit.
- Thus, each hydrogen atom achieves a stable electron structure like the noble gas helium (Figure 5.8).

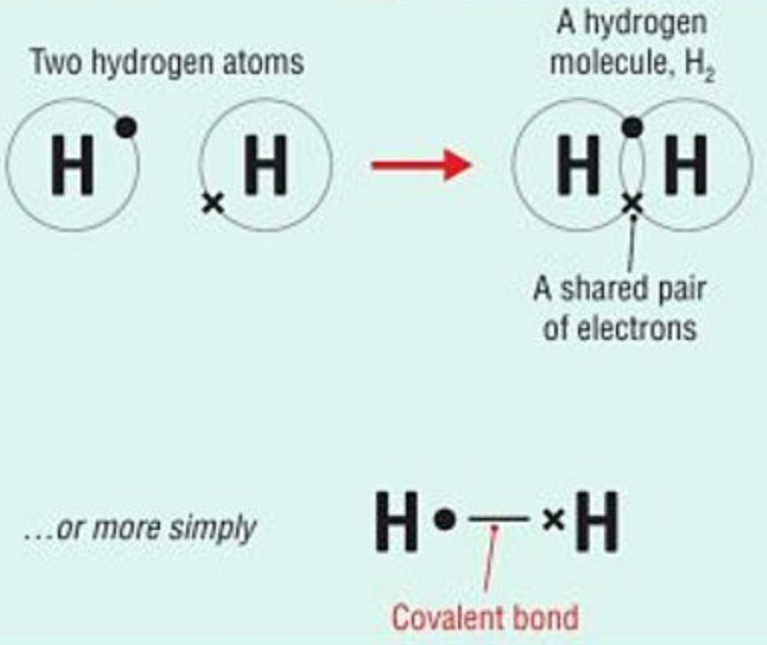


Figure 5.8 Covalent bond formation in a molecule of hydrogen.

The shared pair of electrons in a covalent bond is often represented simply by a dash. Thus, H–H represents a molecule of hydrogen.

Example 5.12

The Chlorine Molecule, Cl_2

- A chlorine atom has seven electrons in its outer energy level.
- To achieve a stable octet of eight electrons, two chlorine atoms share a pair of electrons with each other, i.e. a covalent bond is formed between the two atoms.
- Each atom has its own seven outer electrons and a share in one of the outer electrons of the other atom.

The Lewis diagram to illustrate the formation of the covalent bond in chlorine is shown in Figure 5.9.

Figure 5.9 In the chlorine molecule, the two atoms are held together by a covalent bond.

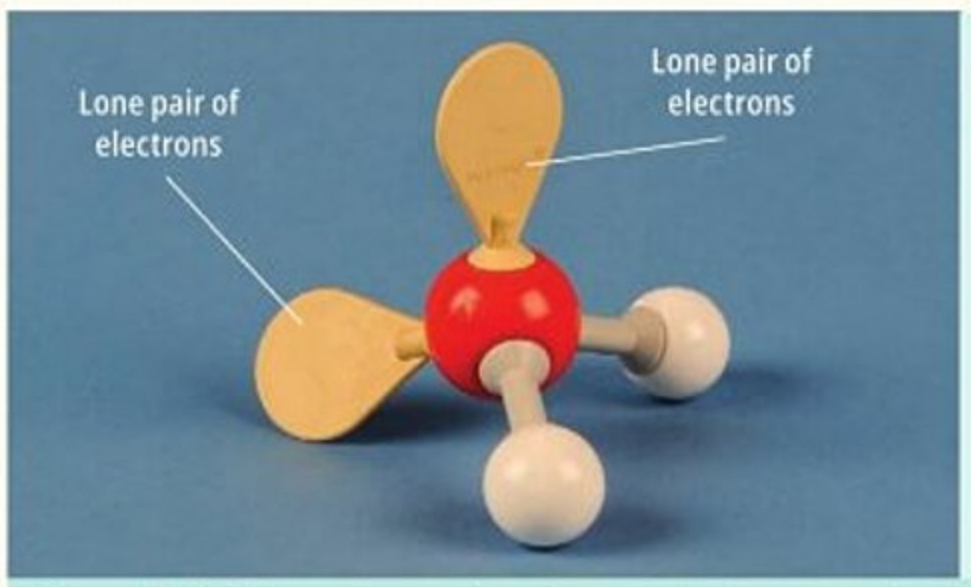
Example 5.13

The Water Molecule, H_2O

- An oxygen atom has six electrons in its outer energy level.
- Therefore, the oxygen atom needs two more electrons to complete its octet.
- To achieve this, the oxygen atom takes a share of one electron from each of two hydrogen atoms. Each hydrogen atom achieves the stable electron configuration of helium, i.e. they have a share of two electrons in each of their outmost orbits.
- Two covalent bonds are formed as shown in Figure 5.10. The water molecule is a V-shaped molecule. We shall understand the reason for this at a later stage.

Note that there are two pairs of electrons on the oxygen atom that are not involved in bonding. These two pairs of electrons are called **'lone pairs'**. They are called 'lone pairs' because they are not bonded to another atom.

Pairs of electrons that **are** involved in bonding (i.e. 'tied up' in covalent bonds) are called **'bond pairs'**. Thus, the oxygen atom in a water molecule has two lone pairs and two bond pairs.



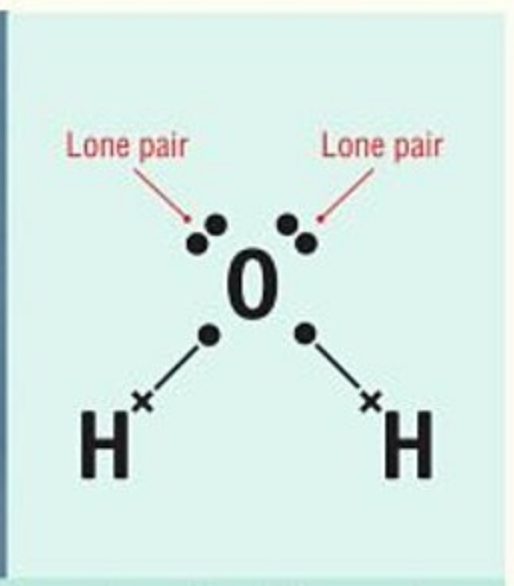


Figure 5.10 The water molecule contains two covalent bonds and two lone pairs.

Example 5.14

The Ammonia Molecule, NH_3

- A nitrogen atom has five electrons in its outer energy level.
- This atom needs three more electrons to complete its octet.
- To achieve this, the nitrogen atom takes a share of one electron from each of three hydrogen atoms. Thus, three covalent bonds are formed as shown in Figure 5.11.

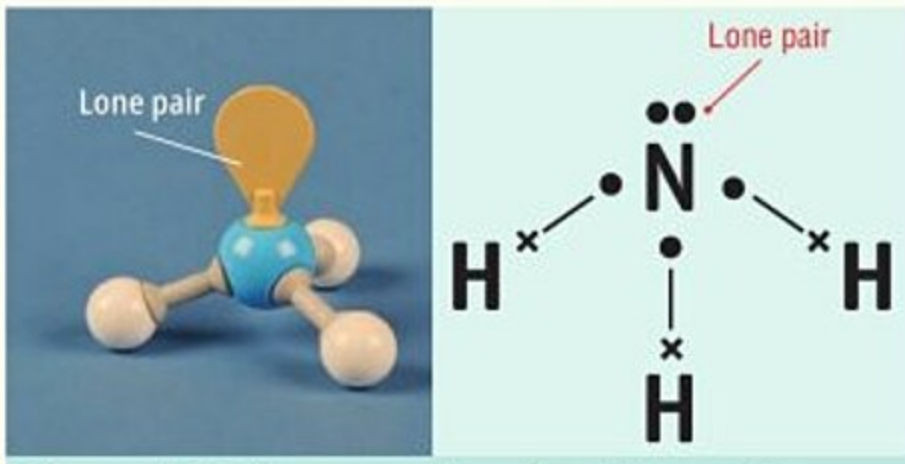


Figure 5.11 The ammonia molecule contains three covalent bonds and one lone pair.

From the above examples, it is clear that one can predict the number of covalent bonds formed around certain atoms:

- Hydrogen atoms form one covalent bond.
- Oxygen atoms form two covalent bonds.
- Nitrogen atoms form three covalent bonds.
- Carbon atoms form four covalent bonds.

The number of covalent bonds formed by atoms of some selected elements is given in Figure 5.13.

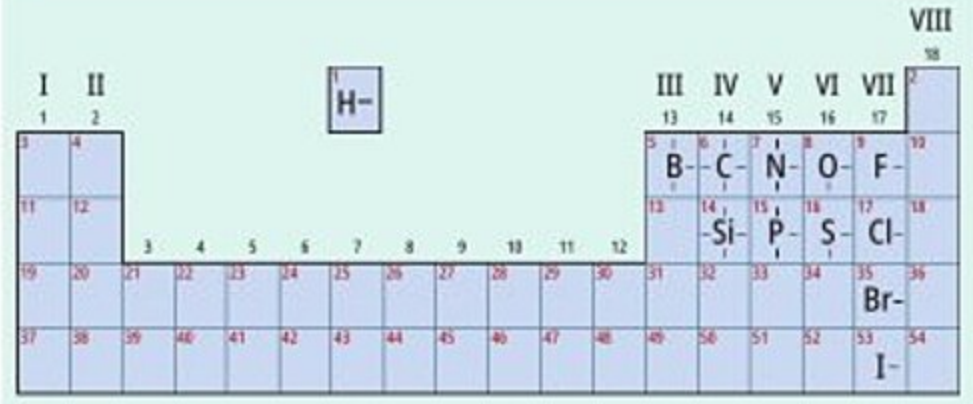


Figure 5.13 The number of covalent bonds formed by atoms of some selected elements that you will commonly encounter on this course. Study this diagram carefully!

Example 5.15

The Methane Molecule, CH_4

- A carbon atom has four electrons in its outer energy level.
- This atom needs four more electrons to complete its octet.
- To achieve this, the carbon atom takes a share of one electron from each of four hydrogen atoms.
- Thus, four covalent bonds are formed as shown in Figure 5.12.

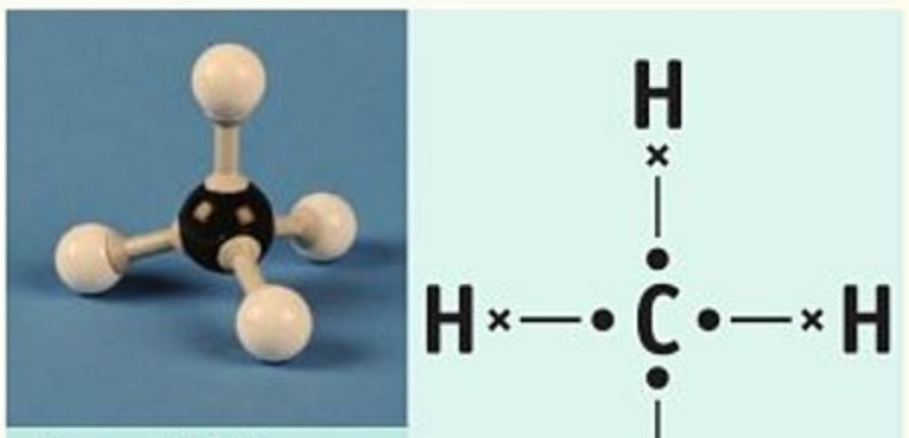


Figure 5.12 The methane molecule contains four covalent bonds.

Since a hydrogen atom cannot combine with more than one atom of any other element, we say its valency ('combining power') is one or it is monovalent. In fact, hydrogen is used as the standard by which valency is measured.

The valency of an element is defined as the number of atoms of hydrogen or any other monovalent element with which each atom of the element combines.

- Therefore, since chlorine combines with one atom of hydrogen (HCl), we say chlorine has a valency of one.
- Since oxygen combines with two atoms of hydrogen, oxygen has a valency of two (H_2O).
- Similarly, nitrogen has a valency of three (NH_3) and carbon a valency of four (CH_4).

Double and triple bonds

In Examples 5.11–5.15, we have seen how atoms shared single pairs of electrons to form covalent bonds. Such bonds are more correctly referred to as **single** covalent bonds.

- A single bond is formed when **one** pair of electrons is shared between two atoms.
- A double bond is formed when **two** pairs of electrons are shared between two atoms. The oxygen molecule contains a double bond and the carbon dioxide molecule contains two double bonds, Figure 5.14.

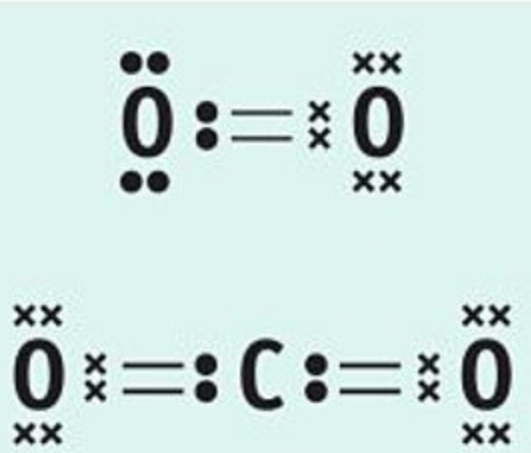


Figure 5.14 Both the oxygen molecule and the carbon dioxide molecule contain double bonds.

- From Figure 5.14, we see that the formation of the double bonds enables each element to achieve the octet of electrons in the outer energy level.
- A triple bond is formed when three pairs of electrons are shared. The nitrogen molecule, N_2, is an example of a molecule that contains a triple bond, Figure 5.15.

Figure 5.15 The nitrogen molecule contains a triple bond.

Example 5.16

Question

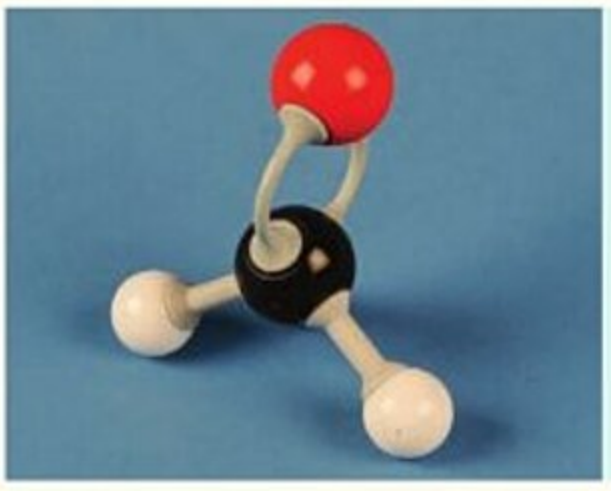
Methanal (more commonly known as formaldehyde) has the formula HCHO. A solution of formaldehyde in water is commonly used in preserving biological specimens.

Draw a Lewis diagram showing the bonding in methanal.

Figure 5.16 Formaldehyde solution is commonly used in preserving biological specimens.

Answer

In showing the bonds in this molecule, remember that each hydrogen atom has just one bond around it, the carbon atom must have four bonds around it, and the oxygen atom has two bonds around it. The valencies of these atoms are satisfied by the structure as shown in Figure 5.17.



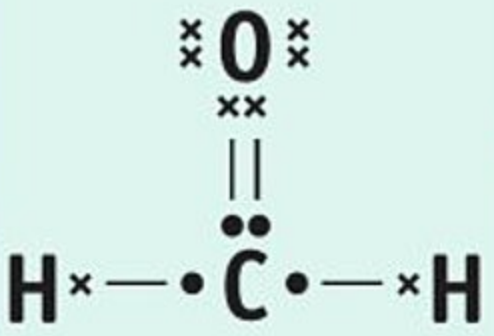


Figure 5.17 The bonding in HCHO shown using the Lewis diagram method.

Sigma and Pi bonding

It is also possible to describe covalent bonding in terms of atomic orbitals.

- The formation of the H_2 molecule can be described by saying that the 1s orbitals of two hydrogen atoms overlap as shown in Figure 5.18.

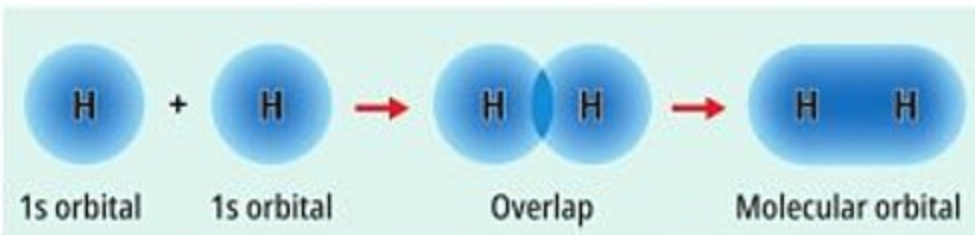


Figure 5.18 The covalent bond in H_2 being formed by the overlap of the 1s atomic orbitals of two hydrogen atoms

- When the two atomic orbitals overlap, they form a **molecular orbital**. This is rather like two soap bubbles coming together to form a larger soap bubble.
- The covalent bond formed by the head-on overlap of the two atomic orbitals is called a **sigma bond**. The Greek letter σ (sigma) is used to indicate a sigma bond.

A **sigma bond** is formed by the head-on overlap of two orbitals.

- The bonding in the chlorine molecule can be explained by overlap of orbitals. If we consider the electron configuration of chlorine, we see that one of its p orbitals is half filled.

$Cl = 1s^2, 2s^2, 2p^6, 3s^2, 3p_x^2, 3p_y^2, 3p_z^1$

- The covalent bond in Cl_2 is formed when two half-filled p_z atomic orbitals (one from each atom) overlap head on to form a sigma bond, Figure 5.19.

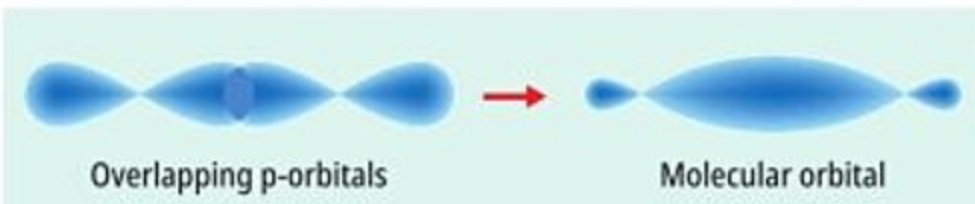


Figure 5.19 The covalent bond in Cl_2 being formed by the head-on overlap of two p orbitals.

- There is very little difference between the orbital approach to single-bond formation and the simple 'shared electron pair' approach as already discussed in Examples 5.11–5.16.
- Both approaches describe the same occurrence, i.e. all single bonds can also be called sigma bonds.

- The two types of description of sigma and pi bonding differ from each other when we look at the formation of double and triple bonds.
- Consider how the double bond in the O_2 molecule is formed.

$O = 1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$

- There are two half-filled p orbitals in the oxygen atom. Imagine two oxygen atoms approaching each other so that the two $2p_y$ orbitals overlap head on to form a sigma bond, Figure 5.20. However, the two p_z orbitals overlap sideways to form what is called a pi (π) bond.
- Therefore, the double bond in oxygen consists of one sigma and one pi bond. This is true of all double bonds.

A **pi bond** is formed by the sideways overlap of p orbitals.

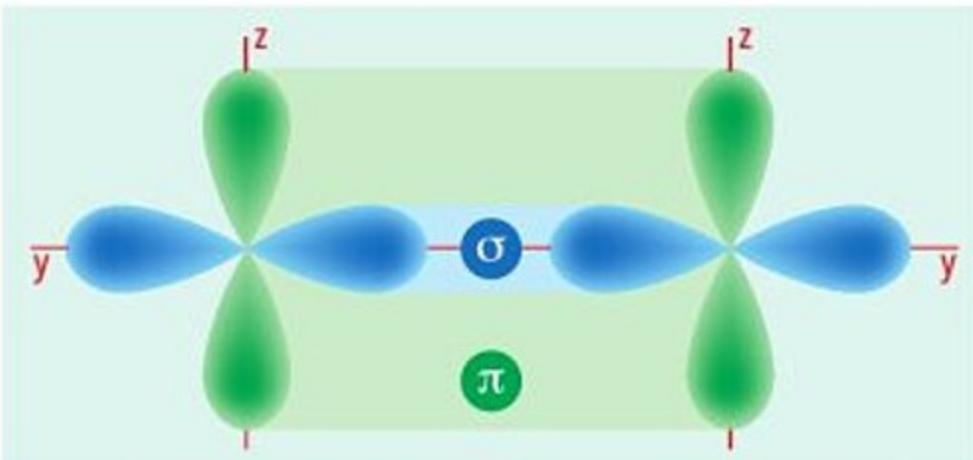


Figure 5.20 The double bond in oxygen consists of one sigma and one pi bond.

Consider how the triple bond in the nitrogen molecule, N_2, is formed.

$N = 1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

There are three half-filled p orbitals in the nitrogen atom. Imagine two nitrogen atoms approaching each other so that the two $2p_x$ orbitals overlap head on to form a sigma bond, Figure 5.21.

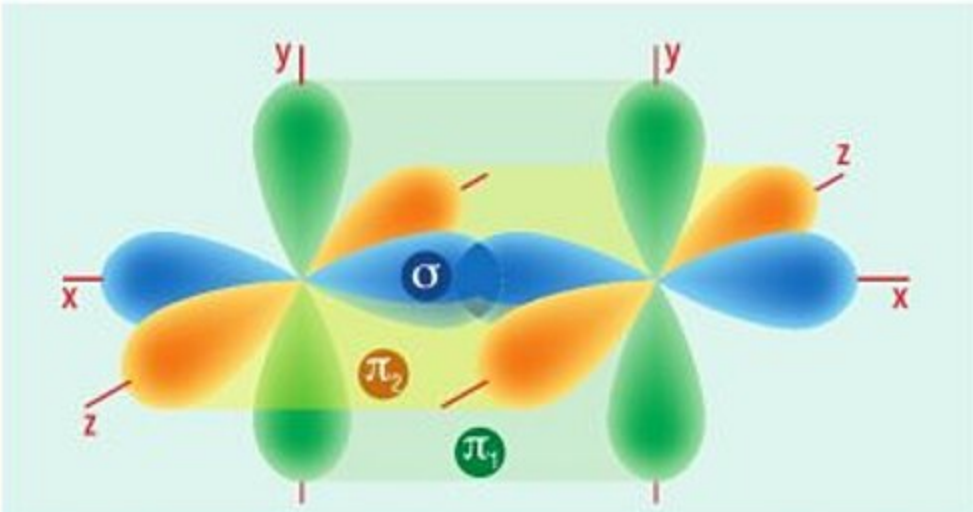


Figure 5.21 The triple bond in nitrogen consists of one sigma and two pi bonds.

We will now consider some examples to help us understand how the VSEPR theory works.

Example 5.17

Beryllium chloride, $BeCl_2$

A molecule of beryllium chloride consists of **two pairs** of electrons around the central atom, Figure 5.23.

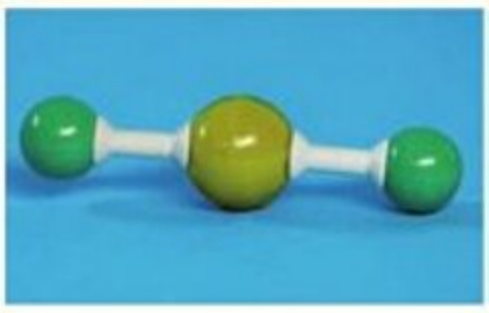


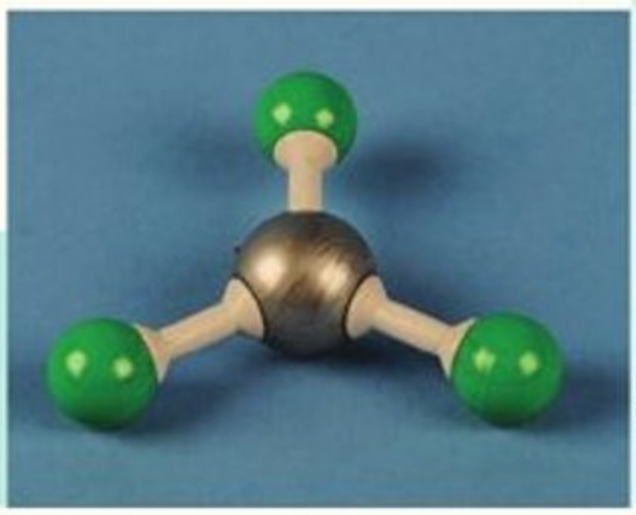
Figure 5.23 In a molecule of beryllium chloride, there are two pairs of electrons around the central atom (i.e. the beryllium atom). The bond angle is 180°.

- The lone pairs of electrons on the chlorine atoms themselves are ignored by the VSEPR theory – we need only consider the electrons that are actually around the central atom.
- By experiment it is found that $BeCl_2$ is a **linear** molecule, i.e. the bond angle is 180°.
- This bond angle is explained by saying that the two pairs of electrons, since they are negatively charged, repel each other and arrange themselves in space as far apart as possible from each other.
- When the bond angle is 180° the repulsion between the pairs is minimised.
- This shape is adopted by any molecule that has two pairs of electrons around the central atom.

Example 5.18

Boron Trichloride, BCl_3

- A molecule of boron trichloride consists of three pairs of electrons around the central atom, Figure 5.24.
- When the bond angle is measured experimentally, it is found to be 120°, i.e. the three pairs of electrons are all equally far apart to minimise repulsion.
- The three pairs of electrons are all in the one plane. Hence, the shape of BCl_3 is said to be **triangular planar** or **trigonal planar**.
- This is the shape adopted by any molecule that has three pairs of electrons around the central atom.



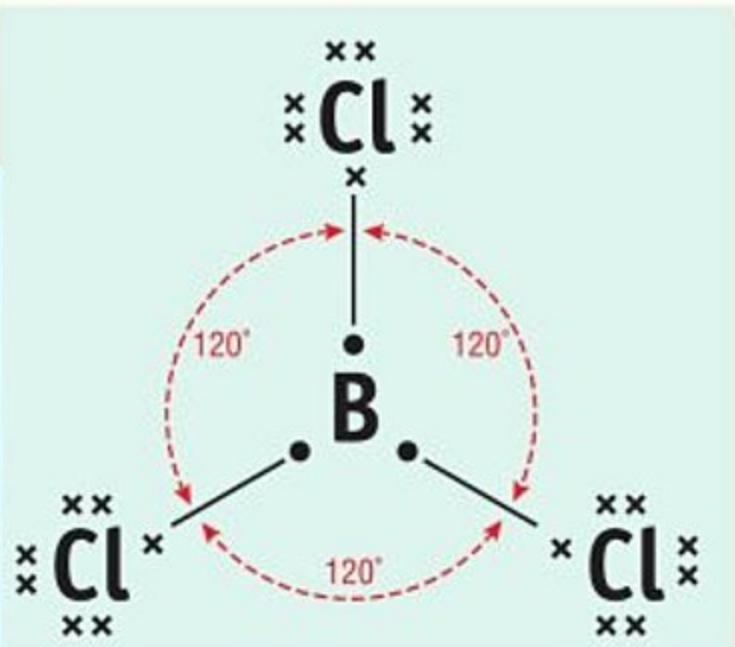


Figure 5.24 The boron trichloride molecule has three pairs of electrons around the central atom. The bond angle is 120°.

- The two $2p_y$ orbitals overlap sideways to form a pi bond.
- A second pi bond is formed from the sideways overlap of the two $2p_z$ orbitals.
- Therefore, the triple bond in nitrogen consists of one sigma and two pi bonds. This is true of all triple bonds.
- In a double bond, one of the bonds is a sigma and one is a pi bond, Figure 5.22.
- Sigma bonds are stronger than pi bonds as there is more overlapping of orbitals in sigma bonds. Therefore, an O=O double bond is not twice as strong as an O–O single bond, since pi bonds are not as strong as sigma bonds.

Figure 5.22 A double bond consists of one sigma and one pi bond. A triple bond consists of one sigma and two pi bonds.

Some differences between sigma and pi bonds are summarised in Table 5.2.

Sigma	Pi
1. Formed by head-on overlap of two orbitals	**1.** Formed by sideways overlap of orbitals
2. Involves any type of orbital (s, p, d, etc.)	**2.** Involves p orbitals (or d orbitals) – cannot involve s orbitals
3. Involves more overlap of orbitals	**3.** Involves less overlap of orbitals
4. Stronger bond which is not easily broken	**4.** Weaker bond which is more easily broken
5. Associated with single covalent bonds	**5.** Associated with double and triple covalent bonds
6. In a multiple bond, formed first and can exist on its own	**6.** Only formed after sigma bond is formed and cannot exist on its own

Table 5.2 Comparing sigma and pi bonding

The orbital theory gives us a detailed picture of the formation of double and triple bonds. This is the only use we will make of this theory in our study of chemistry for the Leaving Certificate. For all other cases of bond description, the simpler description of shared pairs of electrons (the 'shared-pair theory') is perfectly adequate.

5.7 Shapes of covalent molecules

We have already learned that ionic compounds consist of giant crystal lattices, whereas covalent compounds consist of separate molecules. The molecules of covalent compounds have particular shapes. In 1940, Nevil Sidgwick and Herbert Powell, two English chemists, proposed a theory to account for the shapes of molecules. Their theory is known as the **Valence Shell Electron Pair Repulsion Theory** or **VSEPR Theory** for short. The term *valence shell* simply means 'outer energy level'.

The **VSEPR Theory** states the shape of a molecule depends on the number of pairs of electrons around the central atom. Since electrons are negatively charged, the electron pairs repel each other and arrange themselves in space so that they are as far apart as possible.

Example 5.19

Methane CH_4

- In a molecule of methane there are four pairs of electrons around the central atom, Figure 5.25(a).
- When the bond angle is measured experimentally, it is found that it is 109.5°, i.e. the four pairs of electrons take up the shape of a tetrahedron. Note that the molecule is not planar, as all of the atoms do not lie in the same plane.
- By adopting this shape, the repulsion between the four pairs of electrons is minimised.

It is difficult to represent the shape of a tetrahedron on paper. The wedge drawn in Figure 5.25(b) indicates that this particular C–H bond is coming out of the plane of the paper, the C–H dashed line indicates the bond is going behind the paper, and the final two C–H bonds are in the plane of the paper. Examining a model of a tetrahedron, Figure 5.25(c), in your school laboratory will help you understand this.

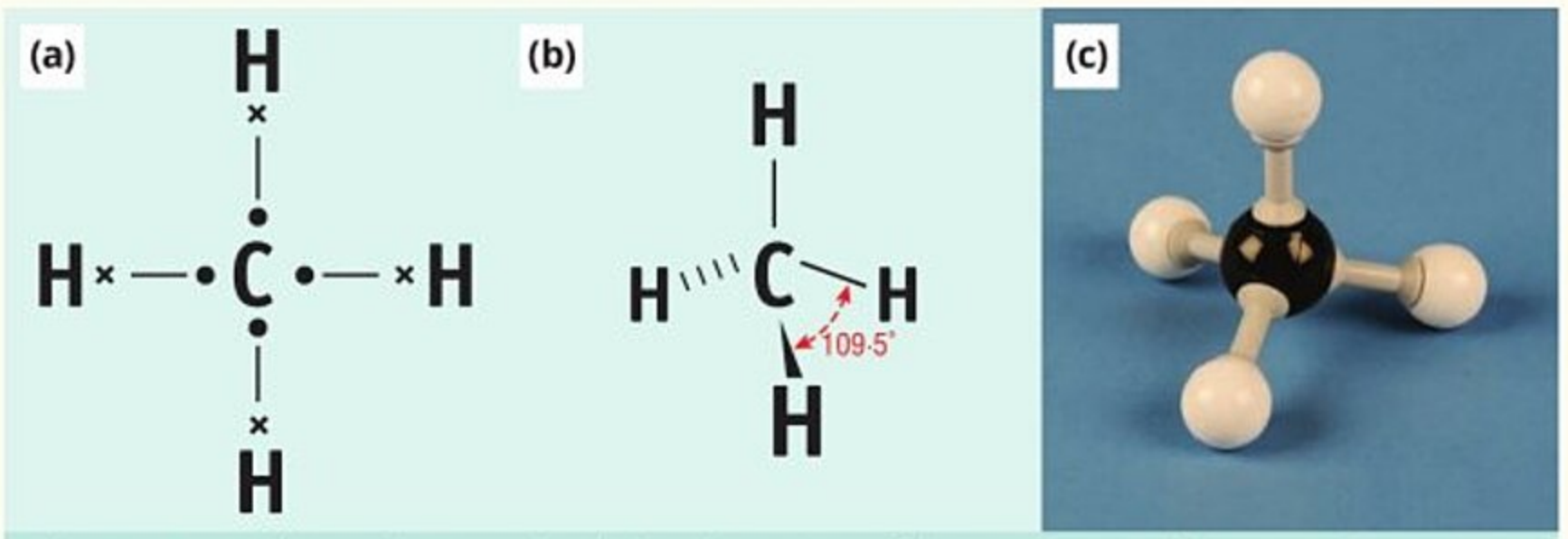


Figure 5.25 (a) The methane molecule has four pairs of electrons around the central atom. The bond angle is 109.5°. (b) Representing a tetrahedron on paper. (c) Model of molecule of methane.

Note that in the three examples above, all pairs of electrons are bond pairs, i.e. there are no lone pairs of electrons in the molecules. A lone pair is a pair of electrons in the outer energy level (orbit) that is not involved in bonding.

- A slight refinement of the VSEPR theory was necessary to take account of the effect of lone pairs on shapes of molecules.
- This modification states that the repulsion between two lone pairs in a molecule is greater than the repulsion between a lone pair and a bond pair, which in turn is greater than the repulsion between two bond pairs: **lone pair/lone pair > lone pair/bond pair > bond pair/bond pair**.
- Since lone pairs are not involved in bonding, they are closer to the nucleus than bond pairs – the electrons in bond pairs spend part of their time near the other atom in the bond.
- Because lone pairs are closer to the nucleus, they exert a greater force of repulsion on each other than bond pairs do. This causes slight differences in the bond angles from the values that would be expected if repulsion was the same for all electron pairs. This is illustrated in Examples 5.20 and 5.21.

Example 5.20

Question

Use the VSEPR theory to deduce the shape of the ammonia molecule, NH_3.

Answer

Step 1

Locate nitrogen in the Periodic Table. It is in Group V (or 15). It has five electrons in its outer energy level.

Step 2

Work out the number of electrons contributed by the three hydrogen atoms to the bonds around the central atom. Since each hydrogen atom contributes one electron, the three hydrogen atoms will contribute a total number of three electrons, Figure 5.26(a).

Step 3

Work out the total number of electron pairs around the central atom.

N	= 5 electrons
3H = 3 × 1	= 3 electrons
Total	= 8 electrons
	= four pairs of electrons
	⇒ tetrahedral shape.

We would therefore predict that ammonia has a regular tetrahedral shape.

- By experiment, it is found that the bond angle in the ammonia molecule is 107°.
- It is less than the regular tetrahedral bond angle of 109.5° due to the presence of the lone pair of electrons.
- The ammonia molecule has one lone pair and three bond pairs of electrons.
- The increased repulsion caused by the presence of the lone pair causes the bond angle to decrease by about 2.5° to 107°, Figure 5.26(a).
- Thus, the shape of the ammonia molecule is **pyramidal**, Figure 5.26(b).

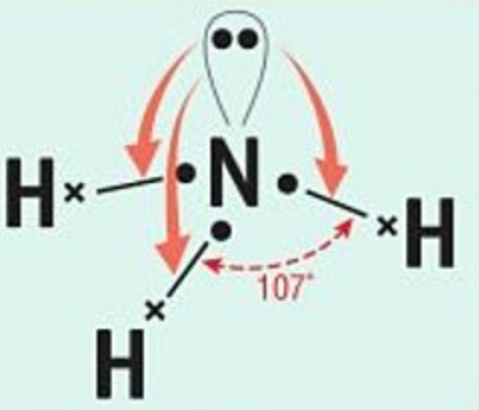


Figure 5.26 (a) Ammonia has the shape of a pyramid.

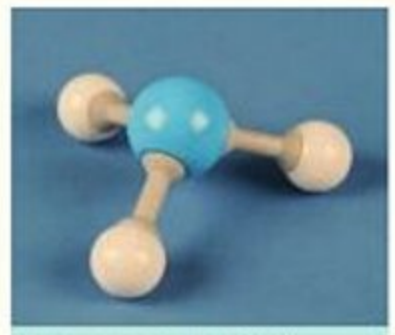


Figure 5.26 (b) Model of ammonia molecule.

Example 5.21

Question

Use the VSEPR theory to deduce the shape of the water molecule.

Proceeding as in Example 5.20.

O	= 6 electrons
2H = 2 × 1	= 2 electrons
Total	= 8 electrons
	= four pairs of electrons
	⇒ tetrahedral shape

- We would predict that the water molecule has a regular tetrahedral shape.
- By experiment, it is found that the bond angle is 104.5°.
- It is less than the regular tetrahedral bond angle of 109.5° because of the presence of the two lone pairs of electrons.
- The water molecule has two lone pairs and two bond pairs of electrons.
- The increased repulsion caused by the presence of the two lone pairs results in the bond angle being decreased by about 5° from 109.5° to 104.5° (Figure 5.27).
- Thus, the shape of the water molecule is **V-shaped**, Figure 5.27.

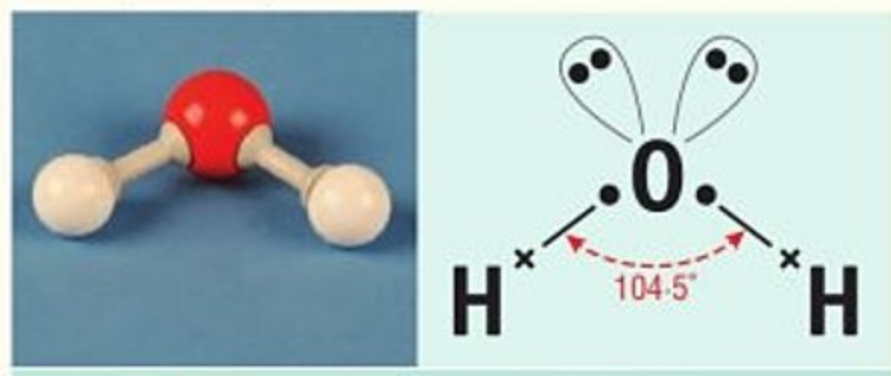


Figure 5.27 The water molecule is V-shaped.

TEST YOURSELF: Attempt Questions 5.2 and W5.3–W5.4.

» Study Examples 5.22, 5.23 and SEC Sample Exam question in the online resources.

5.8 Tests for anions in aqueous solution

We have already seen in Chapter 3 that the presence of positive metal ions in a substance may be detected by means of flame tests. Positive ions are called cations.

A **cation** is a positive ion.

Examples of positive ions that we met in Chapter 3 were Na^+, K^+, Ba^{2+} and Cu^{2+}.

We will now carry out tests to detect the presence of certain negative ions dissolved in water. A solution made by dissolving a substance in water is called an aqueous solution (from the Latin word ***aqua*** for water). In all the following experiments, the negative ions will be dissolved in water. A negative ion is also called an anion.

An **anion** is a negative ion.

The ions we will investigate in this course are:

1. The chloride ion, Cl^-.
2. The sulfate ion, SO_4^{2-} and the sulfite ion, SO_3^{2-}.
3. The carbonate ion, CO_3^{2-} and the hydrogencarbonate ion, HCO_3^-. The old name for the hydrogencarbonate ion was the 'bicarbonate ion'.
4. The nitrate ion, NO_3^-.
5. The phosphate ion, PO_4^{3-}.

You are not required to write fully balanced equations for all of the following tests. In most cases, simple equations involving ions (called **ionic equations**) are perfectly acceptable. You will study the balancing of equations in more detail in Chapter 8.

Note: The type of analysis where we detect the presence of certain substances is known as **qualitative analysis**, i.e. we are determining the presence of a particular substance rather than determining how much of the substance is present.

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook accompanying this textbook.

When you are carrying out laboratory practical work, please ensure that you follow the detailed instructions, including all safety precautions, given in the Student Laboratory Notebook. The points given in Student Experiment 2 summarise the key areas but must not be taken as a substitute for detailed instructions.

5.1 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 2

This Student Experiment is made up of the following five individual experiments:

(i) **Experiment 5.1A:** To detect the presence of chloride ions in aqueous solution.

(ii) **Experiment 5.1B:** To detect the presence of sulfate ions (SO_4^{2-}) and sulfite ions (SO_3^{2-}) in aqueous solution.

(iii) **Experiment 5.1C:** To detect the presence of carbonate ions (CO_3^{2-}) and hydrogencarbonate ions (HCO_3^-) in aqueous solution.

(iv) **Experiment 5.1D:** To detect the presence of nitrate ions (NO_3^-) in aqueous solution.

(v) **Experiment 5.1E:** To detect the presence of phosphate ions in aqueous solution.

5.1A Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook.

Student Experiment No. 2

To detect the presence of chloride ions in aqueous solution

Key steps in procedure

- The chloride salt is dissolved in deionised water.
- A clear solution is obtained.
- A few drops of silver nitrate solution are added to the chloride salt solution.

Observation

- The clear solution turns cloudy.
- A white solid material settles out of solution, Figure 5.30.

This is an example of a precipitation reaction.

A **precipitation reaction** is a reaction in which an insoluble substance is produced from soluble substances in solution. The insoluble substance formed in a precipitation reaction is called the **precipitate**.

Figure 5.30 A white precipitate of silver chloride is formed when silver nitrate solution is added to a solution containing chloride ions.

Explanation

- In this experiment, the precipitate formed is called silver chloride. It is formed when the silver ions from the silver nitrate combine with the chloride ions from the chloride salt that are dissolved in the water.

$$Ag^+ + Cl^- \rightarrow AgCl \downarrow$$

- The arrow pointing down as shown indicates a precipitate is formed.
- The cloudiness is observed because the silver chloride formed does not dissolve in water.

Confirmatory test

- To confirm that the white precipitate is silver chloride, dilute ammonia solution is added to the cloudy solution.

Observation

- The cloudiness disappears.

Explanation

- Silver chloride is soluble in dilute ammonia solution.

Conclusion

- Chloride ions were present in solution.

Note: In chemistry, the substances which cause a chemical reaction to take place are referred to as **reagents**, e.g. in the above reaction, silver nitrate is a reagent. Full details of all the reagents needed for each experiment are given in the Student Laboratory Notebook.

5.1B Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook.

Student Experiment No. 2

To detect the presence of sulfate ions (SO_4^{2-}) and sulfite ions (SO_3^{2-}) in aqueous solution

Key steps in procedure

- A sulfate salt and a sulfite salt are dissolved in deionised water in separate test-tubes.
- A clear solution is obtained in each test-tube.
- A few drops of barium chloride solution are added to each solution.

Observation

- The clear solution in each test-tube turns cloudy.
- White solid materials settle out of the solutions, Figure 5.31.

Figure 5.31 A white precipitate is formed when barium chloride solution is added to a solution of sulfate or sulfite ions.

Explanation

- The insoluble material formed is either barium sulfate or barium sulfite. These compounds are formed when the barium ions from the barium chloride solution combine with the sulfate ions and the sulfite ions dissolved in the water.

$$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$$

barium sulfate

and

$$Ba^{2+} + SO_3^{2-} \rightarrow BaSO_3 \downarrow$$

barium sulfite

To distinguish between sulfate and sulfite ions

- Dilute hydrochloric acid is added to each of the above test-tubes containing the white precipitates.

Observation

- The cloudy precipitate remains in the test-tube that contained the sulfate ions.
- The cloudiness disappears in the test-tube that contained the sulfite ions.

Explanation

- Barium sulfate is insoluble in dilute HCl.
- Barium sulfite dissolves in dilute HCl – or, more correctly, it reacts with dilute HCl. Therefore, the cloudiness disappears in the case of the sulfite ion and remains in the case of the sulfate ion.

$$BaSO_4 + HCl \rightarrow \text{no reaction}$$

$$\underset{\text{barium sulfite}}{BaSO_3} + \underset{\text{hydrochloric acid}}{2HCl} \rightarrow \underset{\text{barium chloride}}{BaCl_2} + \underset{\text{sulfur dioxide}}{SO_2} + \underset{\text{water}}{H_2O}$$

$$\text{i.e. } SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$$

Conclusion

- Sulfate and sulfite ions are detected using barium chloride solution.
- Sulfate and sulfite ions are distinguished from each other using dilute hydrochloric acid solution.
- Barium sulfate is insoluble in dilute hydrochloric acid but barium sulfite is soluble.

5.1C Experiment

Student Experiment No. 2

Full details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook.

To detect the presence of carbonate ions (CO_3^{2-}) and hydrogencarbonate ions (HCO_3^-) in aqueous solution

Key steps in procedure

- The carbonate salt is placed in a boiling tube.
- A one-holed rubber stopper is inserted into the boiling tube.
- The apparatus shown in Figure 5.32 is set up.
- The one-holed rubber stopper is removed and dilute hydrochloric acid is added to the carbonate salt in the boiling tube.
- The one-holed rubber stopper is replaced.

Observation

- A brisk effervescence (fizzing) is observed as the acid comes in contact with the carbonate.
- The gas given off is seen bubbling through the limewater.
- The limewater turns a milky colour.

Explanation

The fizzing is caused by the carbonate ions reacting with the acid to give off a gas:

$$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$$

- The fact that the limewater turns milky shows that the gas is carbon dioxide. Carbon dioxide reacts with limewater to form chalk (limestone). The chemical name for chalk is calcium carbonate.

$$\underset{\text{limewater}}{Ca(OH)_2} + CO_2 \rightarrow \underset{\substack{\text{chalk}\\(\text{limestone})}}{CaCO_3\downarrow} + H_2O$$

Note: If you continue to bubble carbon dioxide through the limewater, the milky colour disappears. This is because the insoluble calcium carbonate eventually reacts with the carbon dioxide to form soluble calcium hydrogencarbonate.

$$\underset{\text{insoluble}}{CaCO_3} + CO_2 + H_2O \rightarrow \underset{\text{soluble}}{Ca(HCO_3)_2}$$

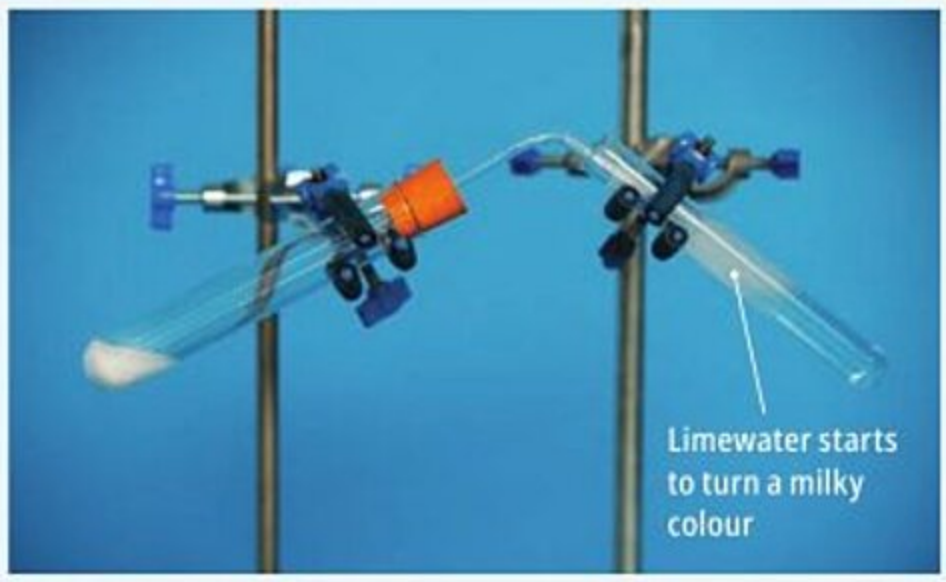

Limewater starts to turn a milky colour
Bubbles of carbon dioxide
Carbonate or hydrogencarbonate salt + dilute HCl
Limewater

Figure 5.32 Carbon dioxide is given off when dilute hydrochloric acid is added to a carbonate or a hydrogencarbonate compound. The carbon dioxide turns limewater milky.

- If the experiment is repeated using a hydrogencarbonate salt instead of the carbonate salt, the same results are obtained. As in the case of the carbonate, the hydrogencarbonate reacts with the acid to liberate carbon dioxide.

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

Conclusion

- Both carbonate ions and hydrogencarbonate ions react with dilute hydrochloric acid to give off carbon dioxide gas.

This effervescence is also observed when you add substances such as *Alka-Seltzer* to water. These are substances that contain sodium hydrogencarbonate and citric acid. When dissolved in water, the citric acid reacts with the hydrogencarbonate to give off carbon dioxide. This causes the fizzing to occur.

5.1C Experiment

To distinguish between carbonate and hydrogencarbonate ions

- Magnesium sulfate ($MgSO_4$) solution is added to solutions of the carbonate salt and the hydrogencarbonate salt in separate test-tubes.
- A white precipitate is formed in the solution containing the carbonate.
- No precipitate is formed in the solution containing the hydrogencarbonate, Figure 5.33.

Explanation

- In the solution of the carbonate, a white precipitate of insoluble magnesium carbonate is formed.

$$Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \downarrow$$
Insoluble

- In the solution of the hydrogencarbonate salt, no precipitate is formed, as magnesium hydrogencarbonate is soluble in water.

$$Mg^{2+} + 2HCO_3^- \rightarrow Mg(HCO_3)_2$$
Soluble

- If the clear solution of magnesium hydrogencarbonate is boiled, a white precipitate of magnesium carbonate appears.

$$Mg(HCO_3)_2 \rightarrow MgCO_3 \downarrow + CO_2 + H_2O$$
Soluble Insoluble

Conclusion

- Carbonate and hydrogencarbonate ions are distinguished from each other using magnesium sulfate solution.
- Magnesium sulfate solution added to a solution containing carbonate ions gives a white precipitate. Magnesium sulfate solution added to a solution containing hydrogencarbonate ions gives a clear solution.
- Magnesium carbonate is insoluble in water but magnesium hydrogencarbonate is soluble.

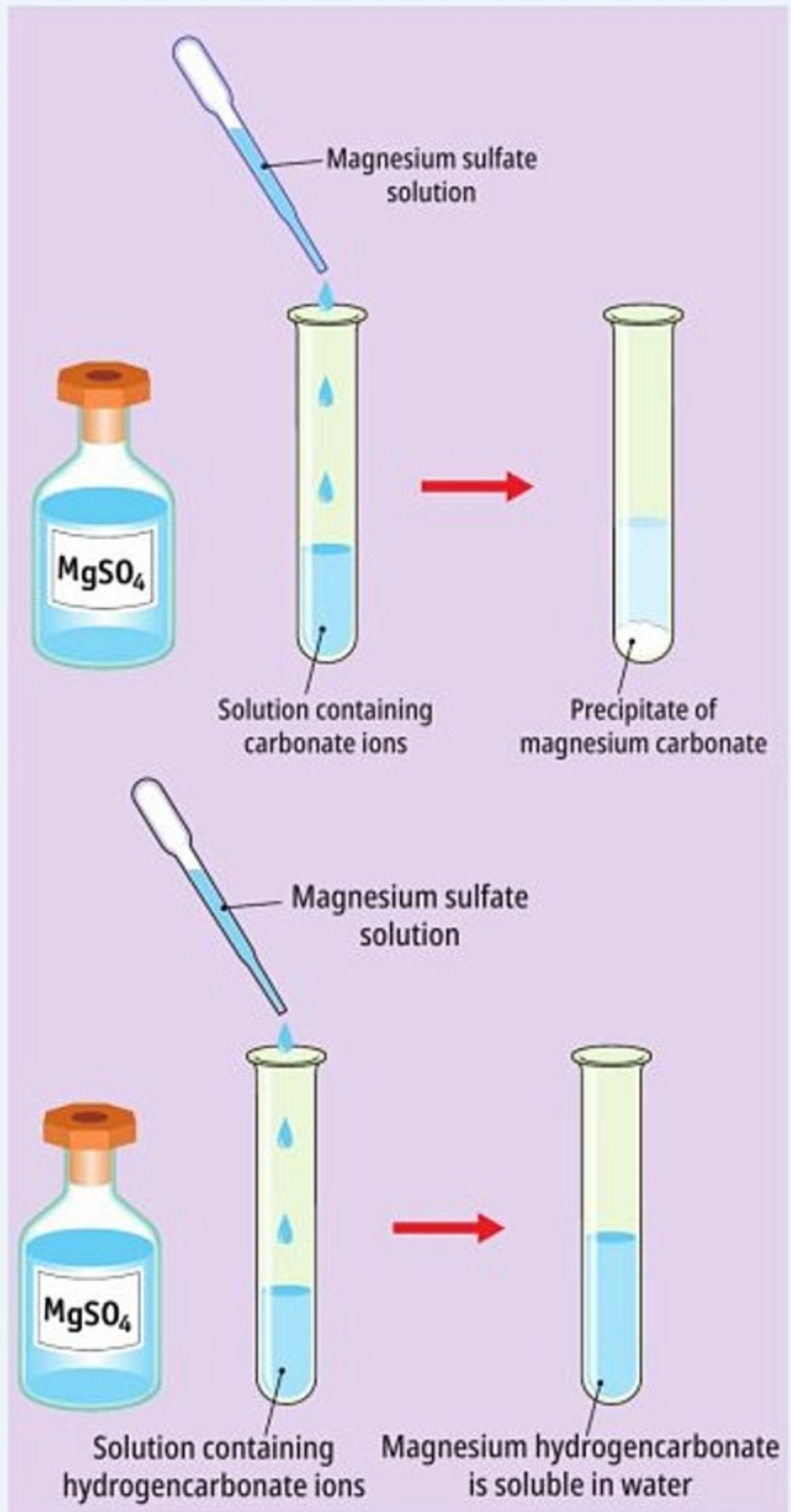


Figure 5.33 A solution of magnesium sulfate is used to distinguish between carbonate and hydrogencarbonate ions.

5.1D Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook.

Student Experiment No. 2

To detect the presence of nitrate ions (NO_3^-) in aqueous solution

Since all nitrate salts are soluble in water, it is not possible to detect the presence of the nitrate ion by a precipitation reaction. A special test called the Brown Ring Test is used to detect the presence of the nitrate ion.

Key steps in procedure

- A nitrate salt is dissolved in deionised water in a test-tube.
- Freshly prepared iron(II) sulfate solution, $FeSO_4$, is added to the solution in the test-tube.
- Using a dropper, concentrated sulfuric acid, H_2SO_4, is added down the inside of the test-tube. The test-tube is slanted slightly as shown in Figure 5.34. Since the concentrated sulfuric acid is so dense, it settles at the bottom of the test-tube and forms a layer underneath the mixture.

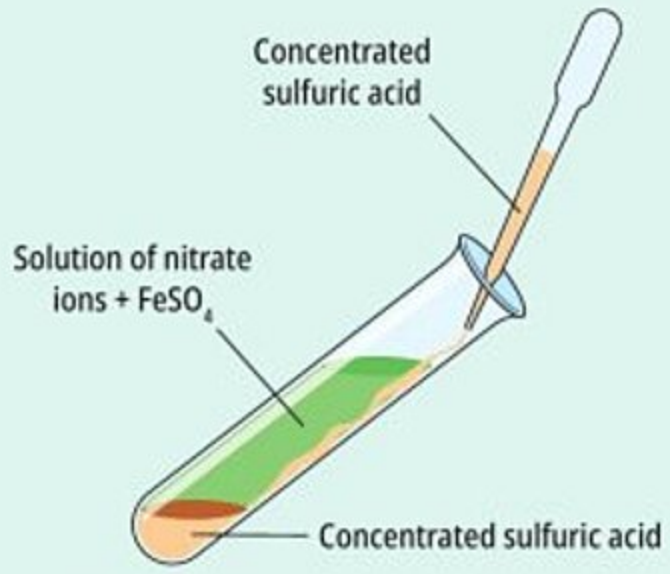


Figure 5.34 Adding concentrated sulfuric acid to the mixture of nitrate ion solution and iron(II) sulfate solution.

Observation

- A brown ring is formed at the junction of the two layers, Figure 5.35.

Explanation

- The brown ring is formed as a result of nitrate ions being present, and hence is the confirmatory test for the presence of the nitrate ion.
- The brown colour is due to the formation of the substance $FeSO_4.NO$.
- When describing this experiment, it is important that you use the phrase ***concentrated* sulfuric acid** as this experiment does not work with dilute sulfuric acid.

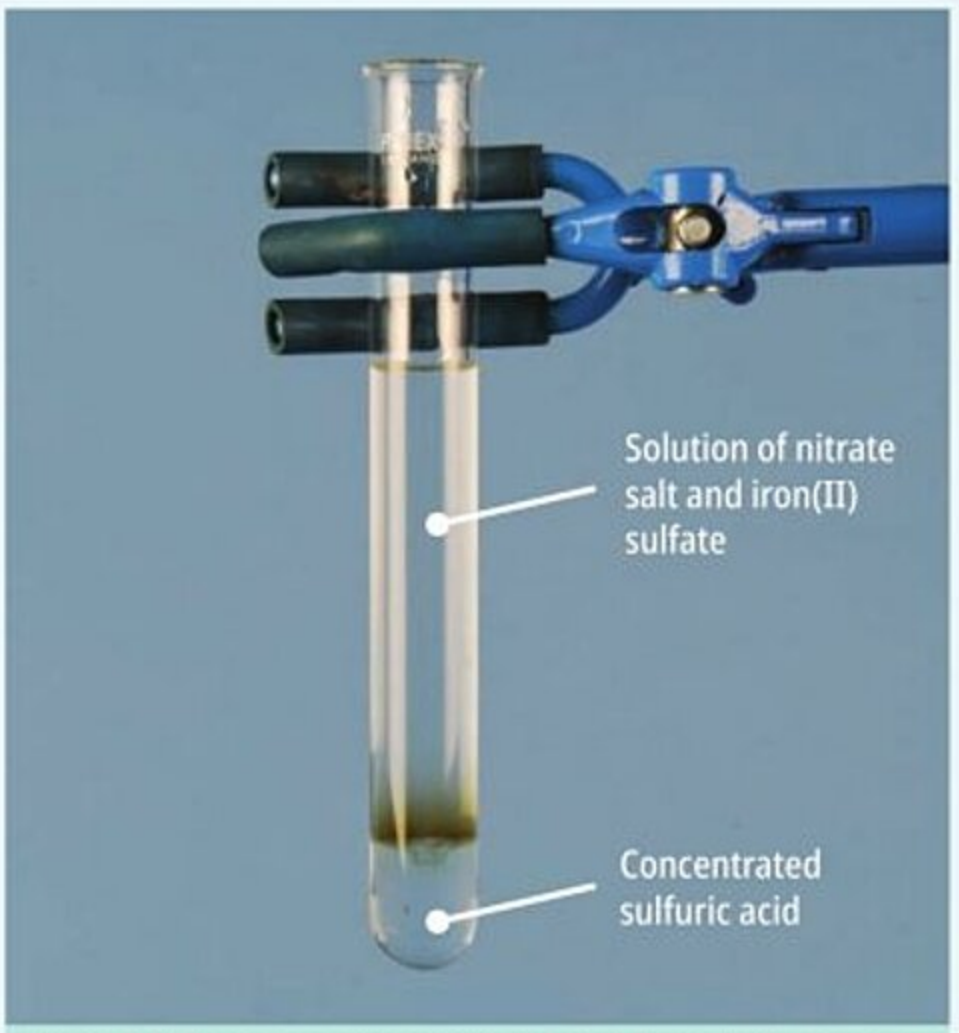


Figure 5.35 A brown ring is formed at the junction between the concentrated sulfuric acid at the bottom and the mixture of the nitrate ion solution and iron(II) sulfate solution on top.

Conclusion

- Nitrate ions are present in the solution.

5.1E Experiment

Student Experiment No. 2

Full details of the procedure for carrying out this experiment are given in Experiment 2 in the Student Laboratory Notebook.

To detect the presence of phosphate ions in aqueous solution

Key steps in procedure

- A phosphate salt is dissolved in deionised water in a test-tube.
- Ammonium molybdate solution is added. Ammonium molybdate is a compound of molybdenum (element number 42 in the Periodic Table). The chemical formula for ammonium molybdate is $(NH_4)_2MoO_4$.
- Using a dropper, a few drops of concentrated nitric acid are added to the test-tube.
- The test-tube is placed in warm water.

Observation

- A yellow precipitate is formed, Figure 5.36.

Explanation

- The yellow precipitate is a substance called ammonium phosphomolybdate.

Conclusion

- Phosphate ions are present in solution.

Figure 5.36 A yellow precipitate is obtained when concentrated nitric acid is added to a solution containing phosphate ions and ammonium molybdate.

The tests for the various ions on your course are summarised in Table 5.3.

DIGITAL: A Folens video of this Student Experiment is available online.

Chapter Summary			
Anion	**Test**	**Observation**	**Inference**
1. Chloride	Add a few drops of $AgNO_3$ solution to a solution of the solid.	A white precipitate is formed which is soluble in dilute ammonia solution.	$Ag^+ + Cl^- \rightarrow AgCl \downarrow$
2. Sulfate or **3.** Sulfite	Add $BaCl_2$ solution to a solution of the solid. Distinguishing test. Add dilute HCl.	A white precipitate is formed. If precipitate remains ⇨ sulfate. If precipitate dissolves ⇨sulfite.	$Ba^{2+} + SO_4^{2-} \rightarrow BaSO_4 \downarrow$ $Ba^{2+} + SO_3^{2-} \rightarrow BaSO_3 \downarrow$ $BaSO_4 + HCl \rightarrow$ no reaction $SO_3^{2-} + 2H^+ \rightarrow SO_2 + H_2O$
4. Carbonate or **5.** Hydrogen-carbonate	Add dilute HCl to the solid. Distinguishing test. Add $MgSO_4$ solution to a fresh solution of the solid.	Fizzing. A gas is given off that turns limewater milky. White precipitate forms ⇨ carbonate. No precipitate forms ⇨ hydrogencarbonate. Boiling gives a precipitate.	$CO_3^{2-} + 2H^+ \rightarrow CO_2 + H_2O$ $HCO_3^- + H+ \rightarrow CO_2 + H_2O$ $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 \downarrow + H_2O$ $Mg^{2+} + CO_3^{2-} \rightarrow MgCO_3 \downarrow$ $Mg^{2+} + 2HCO_3^- \rightarrow Mg(HCO_3)_2$ $Mg(HCO_3)_2 \rightarrow MgCO_3 \downarrow + CO_2 + H_2O$
6. Nitrate	Brown Ring test. To a solution of the solid add a freshly prepared $FeSO_4$ solution. Add concentrated sulfuric acid.	A brown ring is formed at the junction of the two layers. ⇨nitrate ion present	Brown ring is due to presence of nitrate ion.
7. Phosphate	Ammonium molybdate is added to a solution of the solid. Concentrated nitric acid is added. Solution is warmed.	Yellow precipitate is formed.	Phosphate ions are present.

Table 5.3 Summary of tests for anions.

TEST YOURSELF: Attempt Questions 5.3 and W5.5–W5.12.

Summary What I should know

- The octet rule states that when bonding occurs, atoms tend to reach an electron arrangement, with eight electrons in the outermost energy level.
- Ionic bonding involves the complete transfer of electrons from one atom to another. Covalent bonding involves the sharing of electrons.
- A transition metal is one that forms at least one ion with a partially filled d sublevel.
- A sigma bond is formed by the 'head-on' overlap of two orbitals. A pi bond is formed by the sideways overlap of p orbitals.
- The VSEPR theory can be used to predict the shapes of molecules.
- The chloride ion is detected using silver nitrate solution. The confirmatory test is that the cloudy precipitate dissolves in dilute ammonia solution.
- Sulfate and sulfite ions are detected using barium chloride solution. In the case of the sulfate ion, the cloudy precipitate is insoluble in dilute hydrochloric acid. In the case of the sulfite ion, the cloudy precipitate is soluble in dilute hydrochloric acid.
- Carbonate and hydrogencarbonate compounds give off carbon dioxide when dilute acid is added. Carbon dioxide turns limewater milky. The carbonate and hydrogencarbonate ions are distinguished from each other using magnesium sulfate. A precipitate is formed with the carbonate, but not with the hydrogencarbonate.
- The presence of the nitrate ion is confirmed using the brown ring test. The brown ring is formed when concentrated sulfuric acid is added to a solution containing the nitrate compound and freshly prepared iron(II) sulfate.
- The phosphate ion is detected using ammonium molybdate solution and concentrated nitric acid. A yellow precipitate is obtained.

Learning outcomes

At the end of this chapter, I should be able to:			
Describe ionic and covalent bonding.			
Write the formulas of ionic and covalent compounds.			
List some properties of transition metals.			
Distinguish between sigma and pi bonds.			
Apply the VSEPR theory to determine the shapes of molecules.			
Perform tests in the laboratory for the presence of anions in aqueous solution.			

Chapter review questions

5.1

(a) State the octet rule.

(b) Explain the term *ionic bond*.

(c) Give one use of sodium chloride in everyday life.

(d) What is the formula of magnesium bromide?

(e) Transition metals exhibit variable valency. What does this mean?

(f) Name the compound Cu_2O.

(g) How is a transition metal defined?

(h) Why do most transition metal ions have variable valencies?

(i) In the first row of the d-block metals, name one metal which is not normally considered a transition metal.

(j) Write the chemical formulae for: **(i)** silicon chloride, **(ii)** manganese(III) oxide. [LCH]

5.2

(a) What name is give to the chemical bond formed by the sharing of electrons?

(b) What term is used to describe a bond formed by the head-on overlap of atomic orbitals?

(c) Give two general characteristics of covalent compounds.

(d) Draw an 'electron dot' structure showing the bonding in CH_3NCO.

(e) What name is given to a pair of electrons which is not involved in bonding?

(f) How is a pi bond formed?

(g) Give two possible shapes of a covalent molecule with the general formula QX_3. [LCH]

(h) How many **(i)** sigma bonds, **(ii)** pi bonds, result from sharing of the valence electrons between the atoms in a molecule of nitrogen?

(i) What does VSEPR stand for?

(j) How would you describe the shape of **(i)** the ammonia molecule and **(ii)** the $CHCl_3$ molecule?

(k) Predict the two possible shapes of a molecule AB*n* where $n = 2$. [LCH]

(l) In which of the following is the bond angle 180°: NH_3, H_2O, BeH_2, H_2S?

(m) Indicate what shape you would expect each of the following molecules to have: **(i)** PCl_3 **(ii)** CCl_4.

(n) Why is a $BeCl_2$ molecule linear in shape but a H_2O molecule is not? [LCH]

(o) Give two differences between a sigma and a pi covalent bond. [LCH]

5.3

(a) What is an anion?

(b) What is always formed when a chemical reaction occurs?

(c) Write the formulas for the sulfate ion and the sulfite ion.

(d) What term is used to describe a material that settles out of solution?

(e) Is silver chloride soluble in dilute ammonia solution? Describe a test in which this fact is useful.

(f) How would you confirm the presence of sulfite ions in an aqueous solution? [LCH]

(g) What is the formula for silver nitrate?

(h) Name two ions with which barium chloride forms a white precipitate.

(i) Effervescence is observed when a dilute acid is added to a solution containing certain ions. Name the ions.

(j) Write down the equation for the reaction of carbon dioxide with limewater.

(k) Name two reagents used to detect the presence of the nitrate ion in aqueous solution. [LCH]

(l) Identify two reagents needed to test for the presence of phosphate ions in aqueous solution. [LCH]

(m) In testing for the phosphate ion with ammonium molybate solution, what coloured precipitate is obtained?

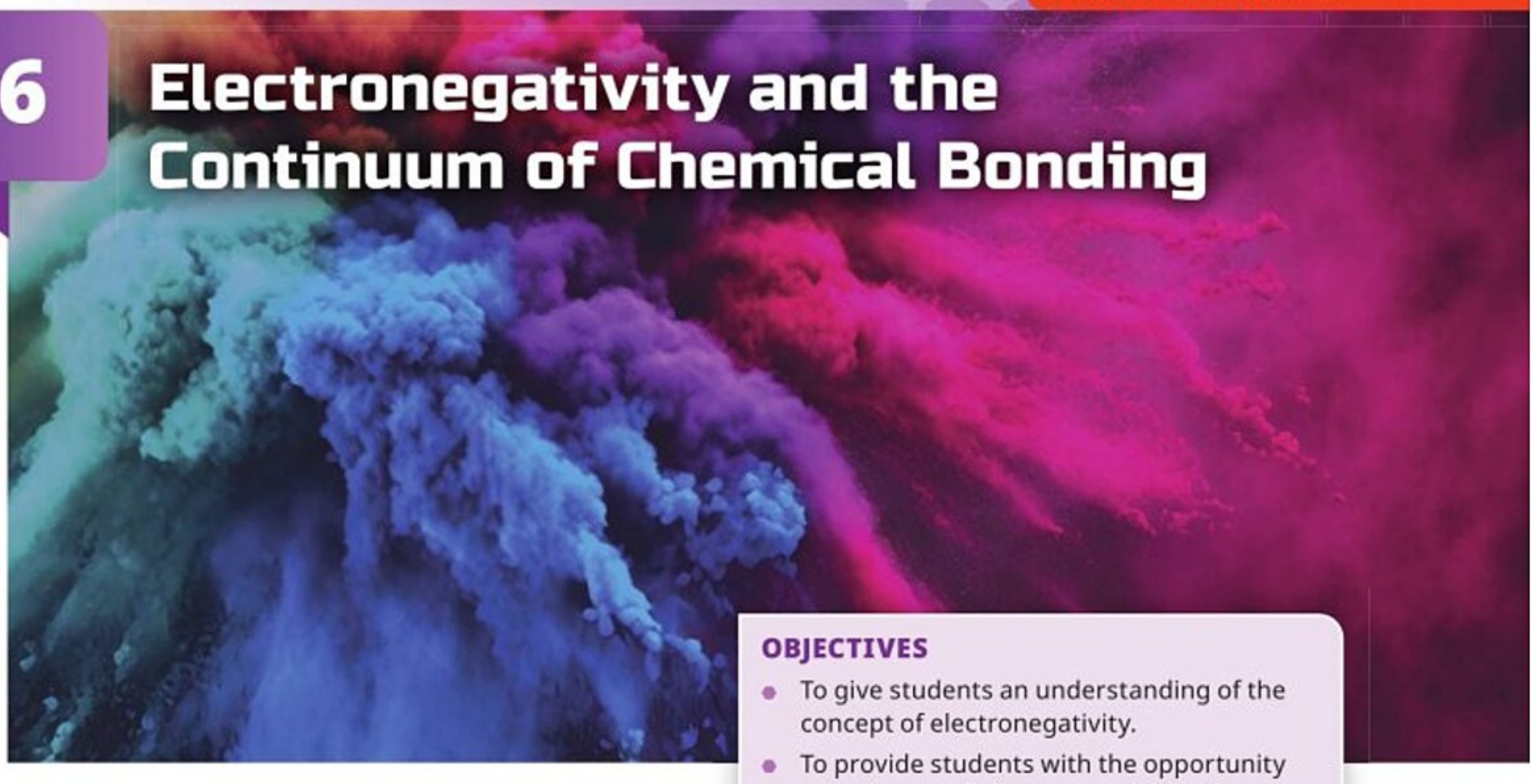
(n) What reagents would you use to test for the presence of chloride ions in aqueous solution? [LCH]

(o) Write an equation for the reaction between a dilute acid and a sulfite. [LCH]

(p) How would you distinguish between sulfite and sulfate ions in aqueous solution? [LCH]

(q) In the brown ring test, name the substance present in the bottom layer in the test-tube. [LCH]

6 Electronegativity and the Continuum of Chemical Bonding



OBJECTIVES

- To give students an understanding of the concept of electronegativity.
- To provide students with the opportunity to make use of electronegativity values to discuss bonding in various compounds.
- To ensure that students know how to interpret the continuum of chemical bonding.
- To make students familiar with a range of intermolecular forces.
- To give students an understanding of the properties of ionic and covalent compounds.

6.1 Introduction

In the last chapter, we studied ionic and covalent bonding. In this chapter, we will complete our study of bonding by looking at ionic and covalent bonding as part of a continuum or spectrum of bonding. We will see that ionic and covalent bonding are at different ends of this spectrum.

In order to understand this continuum of chemical bonding, we will first study an important concept in chemistry called electronegativity.

6.2 Electronegativity: 'Tug-of-war' for electrons

In a covalent bond between identical atoms (e.g. in H_2 or Cl_2), the pair of electrons is shared equally between the two atoms in the molecule. However, chemists have found that in bonds between different atoms, the pair of electrons is often more attracted to one of the atoms than to the other.

- In hydrogen chloride, HCl, it is found that the two electrons in the covalent bond are more attracted to the chlorine than to the hydrogen.
- As the two electrons spend more of their time nearer to the chlorine atom, this gives the chlorine atom a slight negative charge and leaves the hydrogen atom with a slight positive charge.
- This small amount of charge is indicated by the Greek letter δ (delta), Figure 6.1.

Figure 6.1 In the single covalent bond in HCl, the two electrons are more attracted to the Cl atom than to the H atom. This gives the chlorine atom a slight negative charge and the H atom a slight positive charge. This small amount of charge is indicated by the Greek letter δ (delta).

The ability of an atom in a covalent bond to attract the electrons in the bond to itself is given a special name and is called the **electronegativity** of the atom.

Electronegativity is the relative attraction that an atom in a molecule has for the shared pair of electrons in a covalent bond.

Some important points about electronegativity may be summarised as follows:

- Since the 'electron pulling power' of chlorine is greater than that of hydrogen in HCl, we say that chlorine is more electronegative than hydrogen.
- A famous American chemist called Linus Pauling, Figure 6.2, studied the amounts of energy needed to break certain bonds. From his results, he set up a scale of relative values of electronegativity.

For example, he found that fluorine had four times the 'electron pulling power' of calcium. Therefore, he assigned an electronegativity value of 4.0 to fluorine and 1.0 to calcium. A table of electronegativity values is shown in Figure 6.3.

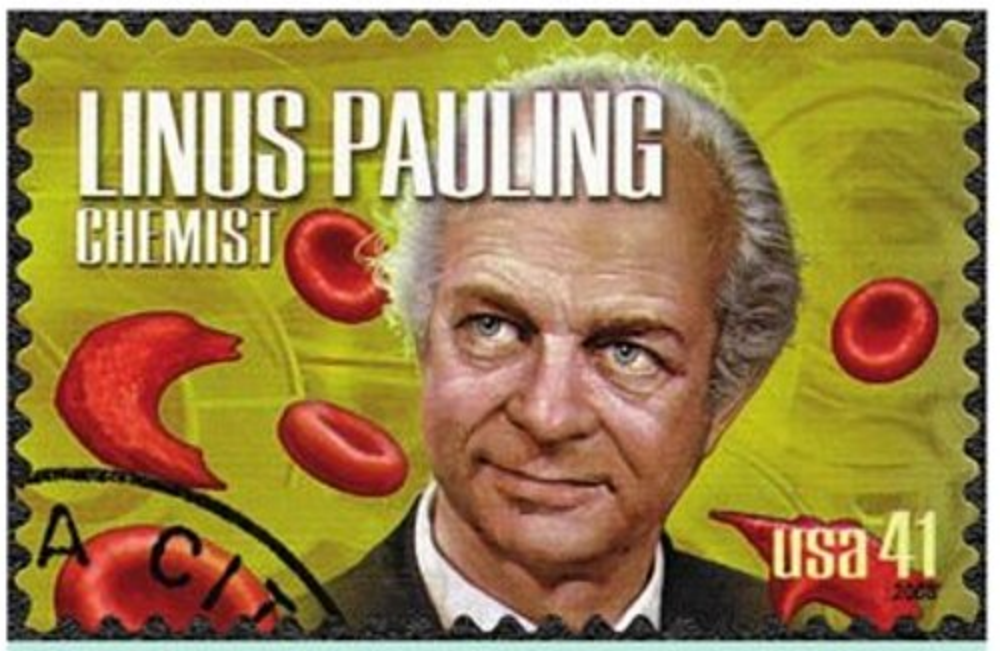


Figure 6.2 In 1939 the American chemist, Linus Pauling, made an enormous contribution to our understanding of chemical bonding in his famous book *The Nature of the Chemical Bond*. In 1954 he was awarded the Nobel Prize in chemistry and he was awarded the Nobel Prize for peace in 1962.

I	II											III	IV	V	VI	VII	0
							H 2·20										He --
Li 0·98	Be 1·57											B 2·04	C 2·55	N 3·04	O 3·44	F 3·98	Ne --
Na 0·93	Mg 1·31											Al 1·61	Si 1·90	P 2·19	S 2·58	Cl 3·16	Ar --
K 0·82	Ca 1·00	Sc 1·36	Ti 1·54	V 1·63	Cr 1·66	Mn 1·55	Fe 1·83	Co 1·88	Ni 1·91	Cu 1·90	Zn 1·65	Ga 1·81	Ge 2·01	As 2·18	Se 2·55	Br 2·96	Kr --
Rb 0·82	Sr 0·95	Y 1·22	Zr 1·33	Nb 1·60	Mo 2·16	Tc 2·10	Ru 2·20	Rh 2·28	Pd 2·20	Ag 1·93	Cd 1·69	In 1·78	Sn 1·96	Sb 2·05	Te 2·10	I 2·66	Xe 2·60
Cs 0·79	Ba 0·89	La 1·10	Hf 1·30	Ta 1·50	W 1·70	Re 1·90	Os 2·20	Ir 2·20	Pt 2·20	Au 2·40	Hg 1·90	Tl 1·80	Pb 1·80	Bi 1·90	Po 2·00	At 2·20	Rn --
Fr 0·70	Ra 0·90	Ac 1·10															

Figure 6.3 Electronegativity values of the elements

- Note from Figure 6.3 that the more electronegative elements are the very reactive non-metals such as fluorine and chlorine. The least electronegative elements are the very reactive metals such as potassium and sodium.
- Elements with low electronegativity values are said to be electropositive.
- Since chlorine is more electronegative than hydrogen, it is more correct to refer to the bond in H–Cl as a polar covalent bond.

A **polar covalent bond** is a bond in which there is unequal sharing of the pair (or pairs) of electrons. This causes one end of the bond to be slightly positive (δ+) and the other end slightly negative (δ-).

Some examples of polar covalent bonds are shown in Figure 6.4.

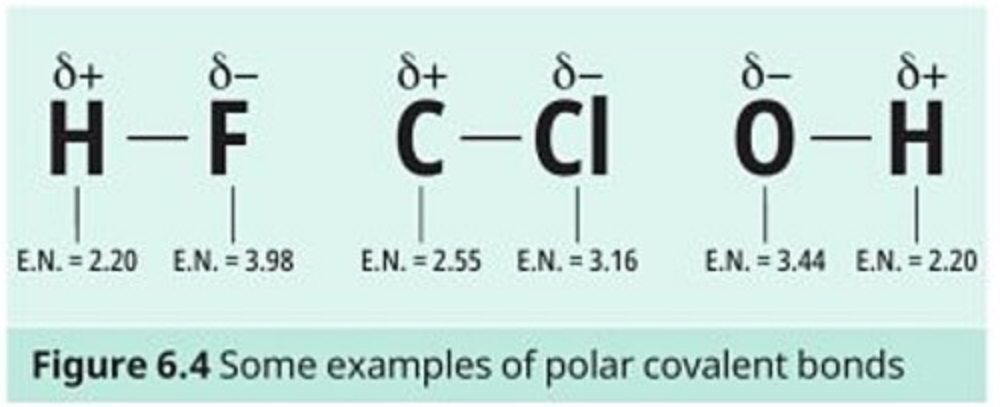


Figure 6.4 Some examples of polar covalent bonds

Pure covalent

The term ***pure covalent*** is often used to refer to a covalent bond where there is equal sharing of the two electrons in the bond.

A **pure covalent bond** is a bond in which there is equal sharing of the pair (or pairs) of electrons. This occurs because the atoms bonded together have identical or very similar electronegativity values, i.e. neither atom exerts a significantly stronger pull on the shared pair or pairs of electrons.

Some examples of pure covalent bonds are shown in Figure 6.5. Note that in the compound PH_3, the P–H bond is considered pure covalent, since the electronegativity values of P and H are virtually identical (2.19 and 2.20 respectively).

Figure 6.5 Some examples of pure covalent bonds

Uses of electronegativity values

There are two main uses of electronegativity values:

1. To predict the polarity of covalent bonds.
2. To predict the type of bonding in a compound.

We now explain both of these uses.

To predict polarity of covalent bonds

By referring to the table of electronegativity values, we can tell if the bonds in a molecule are pure covalent or polar covalent. The greater the electronegativity difference, the more polar the bond, Figure 6.6.

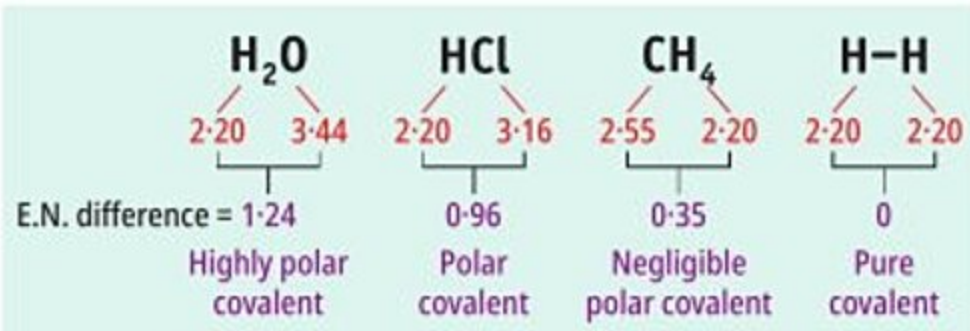


Figure 6.6 The electronegativity difference between the elements in a covalent bond tells us whether the bond is polar covalent or pure covalent.

Polar covalent bonds in polar molecules

In most molecules that have polar covalent bonds, the molecules themselves are also polar.

A **polar molecule** is a molecule that has an uneven distribution of electrical charges. This means that the molecule has regions (poles) with partial positive and partial negative charges separated by a distance.

Polarity in a molecule occurs due to differences in electronegativity between the atoms in the molecule, and also the shape of the molecule, which prevents the charges from cancelling out.

For a molecule to be polar, the following two conditions must be fulfilled:

1. One or more bonds must be polar covalent, i.e. there must be a significant electronegativity difference between the atoms in the molecule.
2. The centres of partial positive and partial negative charges in the molecule must be separated by a distance. This usually occurs when the molecule is asymmetric or lacks uniformity in the balance of charges. In other words, the polar bonds do not cancel each other out.

Examples of polar molecules are hydrogen fluoride (HF), water (H_2O) and ammonia (NH_3), Figure 6.7.

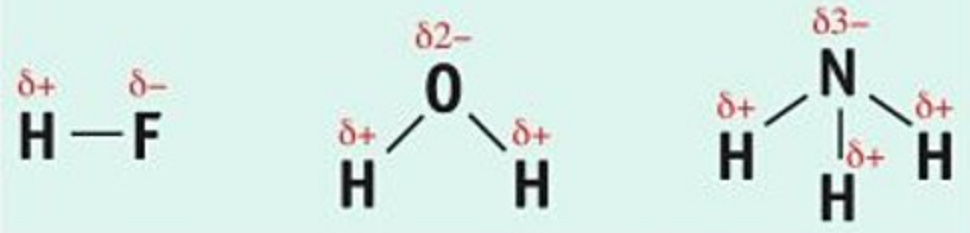


Figure 6.7 Hydrogen fluoride, water and ammonia have polar covalent bonds. Overall, each of these molecules is a polar molecule since the positive and negative poles are separated by a distance. Note that since each molecule is neutral overall, the sum of all the partial charges must add up to zero.

If you examine the shapes of models of each of these three molecules, you will see that the centres of partial positive and partial negative charges (also called positive and negative poles) are separated by a distance.

Note that when representing polar molecules, the sums of all the positive and negative charges must add up to zero.

Polar covalent bonds in non-polar molecules

There are some molecules which, even though they have polar covalent bonds, are not polar molecules.

- It is found that if the shape of the molecule is symmetrical or uniform, the charges cancel each other out. In doing so, the molecule overall is considered to be non-polar. Studying Figure 6.8 will help you to understand this.
- Note that all the molecules in Figure 6.8 are symmetrical. These shapes cause the centre of all the partial positive charges and partial negative charges to coincide and cancel each other out.
- Examining models of these molecules will help you to understand that they are symmetrical. This is explained in more detail in the online videos accompanying this textbook.

The fact that water is a polar molecule gave chemists an indication of the shape of the molecule. If water were linear rather than V-shaped, then it would not be a polar molecule, Figure 6.9.

Note: If there are no polar covalent bonds in a molecule, then the molecule must be non-polar. For example, H_2, N_2 and O_2 are all non-polar molecules.

A **non-polar molecule** is a molecule that has an even distribution of electrical charges due to the symmetry of the molecule. This means that the molecule has regions (poles) with partial positive and partial negative charges that are not separated by a distance but coincide with each other.

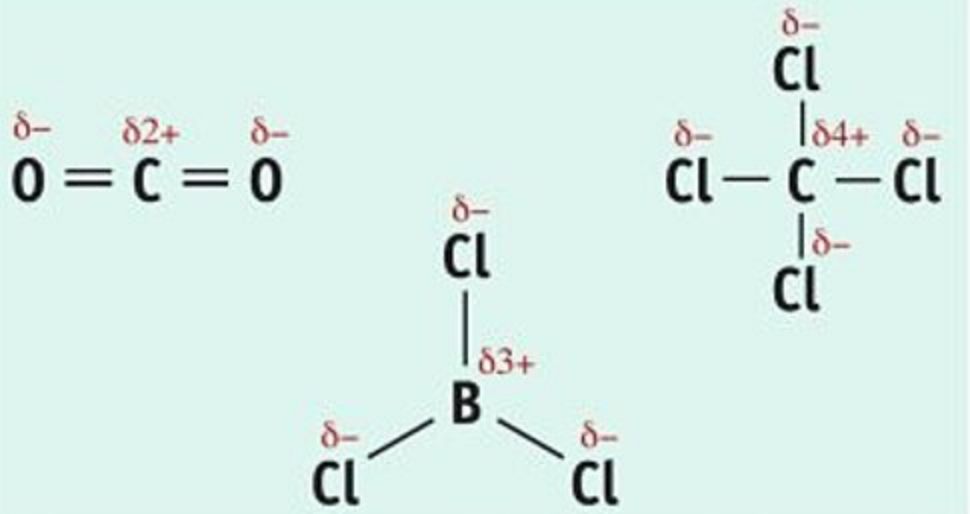


Figure 6.8 In each molecule, the centre of the partial negative charges coincides with that of the partial positive charges. Therefore, none of these molecules are polar molecules.

Figure 6.9 If the water molecule were linear, it would not be a polar molecule. The fact that water is V-shaped means that the partial positive and negative charges do not cancel out, and hence water is a polar molecule.

To demonstrate whether a liquid is polar or non-polar

A simple way of demonstrating whether a liquid is polar or non-polar is to study the effect of a negatively charged plastic rod on a stream of liquid from a burette, Figure 6.10.

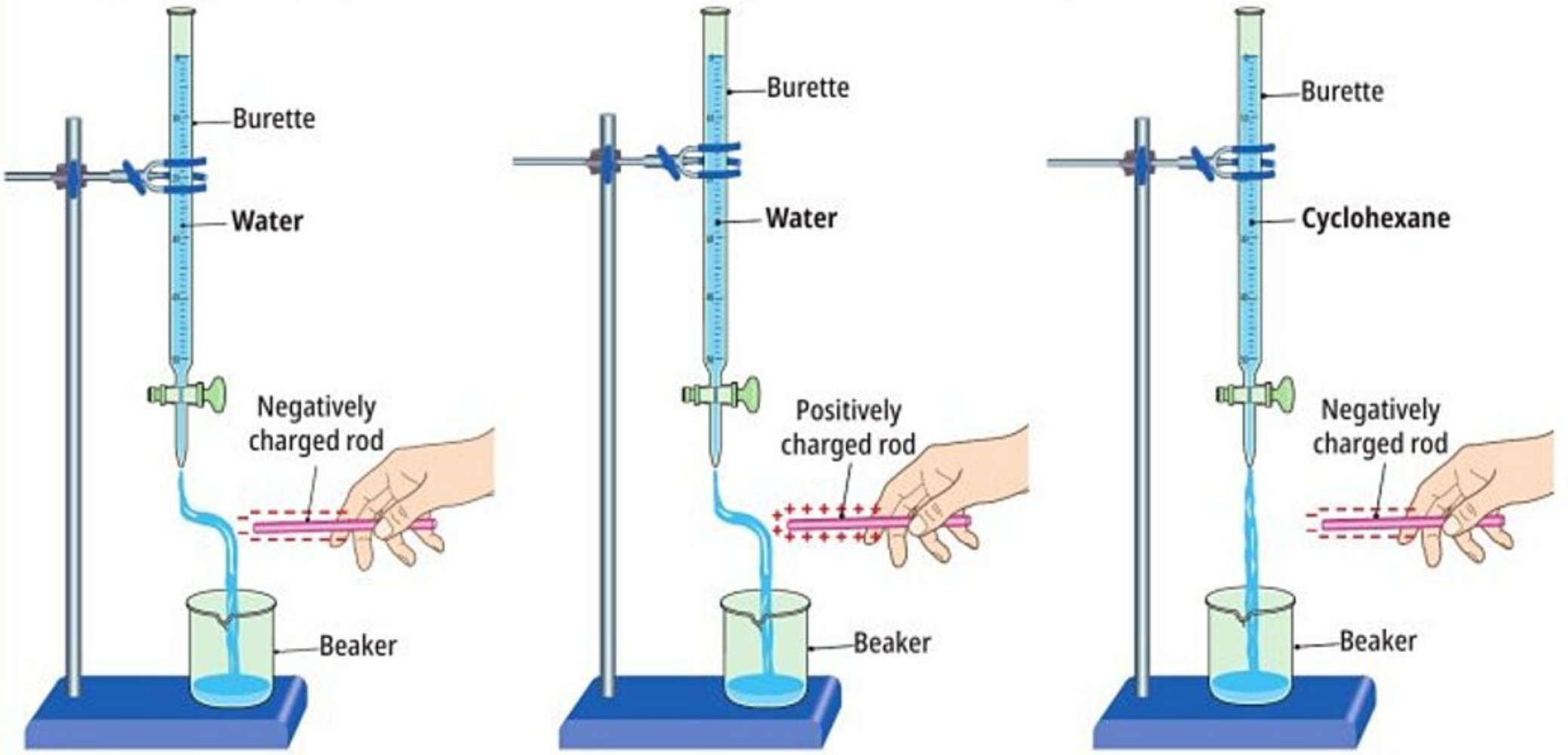


Figure 6.10 A polar liquid (e.g. water) is attracted to the charged rod. The type of charge on the rod does not make any difference to the result of the experiment. A non-polar liquid (e.g. cyclohexane) is not affected by the charged rod.

- If the liquid is a polar liquid (e.g. water), the stream of liquid is attracted to the rod as shown.
- The positive poles of the water molecules are attracted towards the negatively charged rod.
- It does not matter if the negatively charged rod is replaced with a positively charged one. The water will still be attracted to the rod, as the water molecules will turn so that the negative poles of the molecules are attracted to the positively charged rod.
- If the experiment is repeated with a non-polar liquid (e.g. cyclohexane), no attraction is observed, since there are no polar molecules in the liquid.

Note: The fact that water is a polar molecule is the reason why microwave ovens can cook food. These ovens produce electromagnetic waves which change direction millions of times per second. The polar water molecules continuously try to line up with the changing direction of the waves. This causes a lot of friction between the molecules and generates a lot of heat to cook the food., Figure 6.11.

The second use of electronegativity values is to predict the type of bonding in a compound. This will be studied in the next section.

Figure 6.11 The fact that the water molecule is polar helps microwave ovens to cook food.

6.3 The continuum of chemical bonding

The second use of electronegativity values is to predict the type of bonding in a compound. Chemical bonds are often explained using a continuum or spectrum that describes pure covalent, polar covalent and ionic, Figure 6.12.

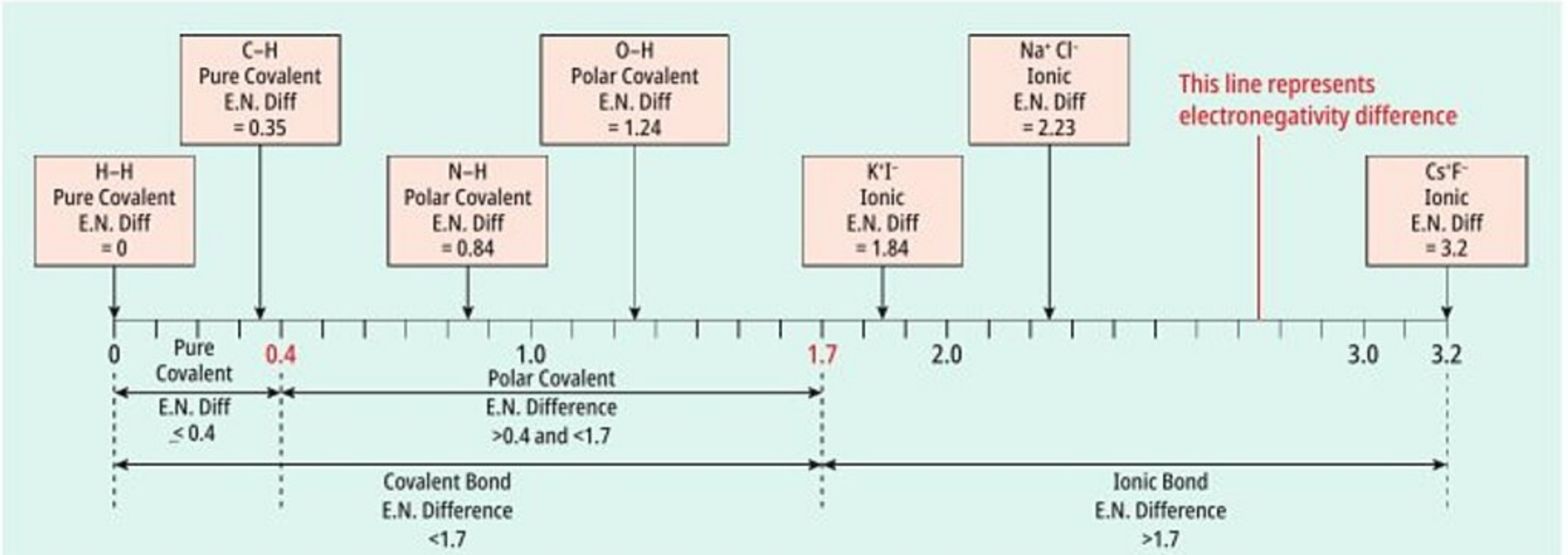


Figure 6.12 The continuum of chemical bonding is represented on a scale marked in units of electronegativity difference.

Study Figure 6.12 carefully and note the following points:

- The scale on the continuum refers to **electronegativity difference** between the two elements that are involved in the bond.
- Note that the continuum ranges from 0 to 3.2.
- The lowest value of electronegativity difference on the continuum is 0. This occurs in pure covalent molecules, e.g. H_2.
- The highest value of electronegativity difference (3.2) occurs in the compound caesium fluoride (Cs^+F^-). If you study the table of electronegativity values in the *SEC Formulae and Tables* booklet, you will see that fluorine is the most electronegative element in the Periodic Table and caesium is the least electronegative element in the Periodic Table. (Francium is ignored as it is an unstable radioactive element.)
- The continuum is divided into two main parts: covalent bonding and ionic bonding.
- The covalent part of the continuum is further sub-divided into **pure covalent** and **polar covalent**.
- Some electronegativity differences are summarised in Table 6.1.

Bond	Electronegativity Difference
H – H	0.00
P – H	0.01
C – H	0.35
S – H	0.38
N – H	0.84
C – O	0.89
B – Cl	1.12
O – H	1.24
K^+I^-	1.84
Li^+Cl^-	2.18
Na^+Cl^-	2.23
Cs^+F^-	3.19

Table 6.1 Some examples of electronegativity differences in chemical bonds between various elements.

There is a useful 'rule of thumb' that summarises the continuum of bonding. A rule of thumb means that this is a method that is a rough guideline but is not a scientific law. This rule of thumb assists us in predicting whether a compound is ionic or covalent, and also the degree of polarity in a covalent bond.

An electronegativity difference **greater than 1.7** indicates **ionic bonding** in a compound.

An electronegativity difference **less than or equal to 1.7** indicates **covalent bonding** in a compound.

An electronegativity difference **greater than 0.4 and less than 1.7** indicates that the covalent bond is **polar covalent**.

An electronegativity difference **greater than zero but less than or equal to 0.4** indicates that the covalent bond is **slightly polar** which, in practice, may be considered **nonpolar**.

An electronegativity difference of zero indicates that the bond is **pure covalent** and, therefore, also **nonpolar.**

For example, consider the electronegativity differences of the elements in potassium fluoride and methane, Figure 6.13.

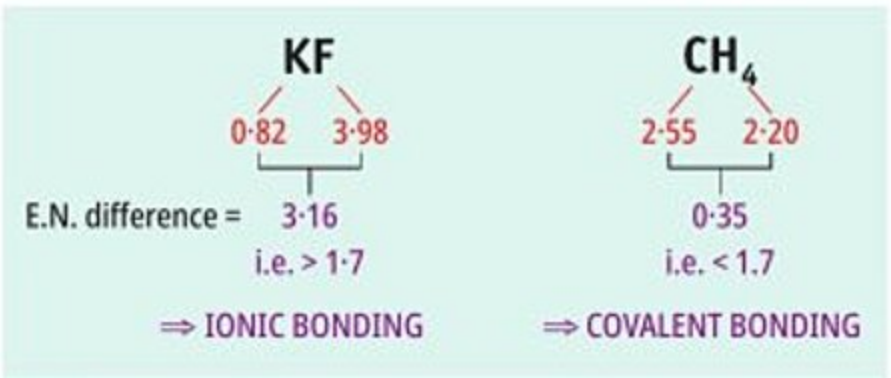


Figure 6.13 Electronegativity differences may be used to predict ionic and covalent bonding.

It is important to remember that the above is not a definite law but simply a rule of thumb, which is useful for predicting the type of bonding that might be expected in a given compound. There are some exceptions to the above rule of thumb.

- The main exceptions are lithium hydride (LiH), sodium hydride (NaH), potassium hydride (KH) and calcium hydride (CaH_2). All these compounds are ionic and contain the hydride ion, H^-. The above rule of thumb would indicate incorrectly that the bonding is covalent.
- The compound HF is also an exception. The electronegativity difference in the H – F bond is 1.78. Therefore, the rule of thumb would suggest that the bonding is ionic. However, HF is a covalent compound.
- Another exception is the covalent compound BF_3. The electronegativity difference in the B – F bond is 1.94. Therefore, the rule of thumb would suggest that the bonding is ionic. However, BF_3 is a covalent compound.

NOTE

Similar to the octet rule, this rule-of-thumb for predicting bonding is another example of a limitation in predicting bonding between atoms.

TEST YOURSELF: Attempt Questions 6.1 and W6.1–W6.2.

Study SEC exam question 6.1 and model answer in the online resources.

6.4 Intermolecular forces

So far we have studied the two main types of bonding: ionic bonding and covalent bonding. Since these types of bonds hold atoms together **inside** or **within** the molecule, this type of bonding is often referred to as **intramolecular** bonding (Latin: *intra* = inside or within). Think of the phrase *INTRAvenous injection*, i.e. where the drug is injected *INSIDE* the vein, Figure 6.14.

There are other types of bonds that exist **between** one molecule and another. These types of bonding are referred to as **intermolecular forces** (Latin: *inter* = between). Think of the word *INTERnet* which allows communication *BETWEEN* people.

Studying Figure 6.15 may help you to understand the difference between intramolecular bonding and intermolecular forces. (Remember that intermolecular forces do not apply to ionic compounds, as ionic compounds consist of ions in a crystal lattice rather than individual molecules.)

Note in Figure 6.15 that intermolecular forces are represented using dashes. (Do not use dots, as these are used to represent electrons). Intramolecular forces in covalent bonds are much stronger than intermolecular forces between molecules. These intermolecular forces of attraction are commonly called **van der Waals forces**, after the Dutch scientist Johannes van der Waals who discovered them, Figure 6.16. In 1910 he was awarded the Nobel Prize in physics for his work on these forces.

Van der Waals forces are weak, intermolecular forces of attraction that exist between all molecules.

Characteristics of van der Waals forces:

- Van der Waals forces are weaker than covalent or ionic bonds.
- They occur between all molecules regardless of the individual characteristics of the molecules (e.g. polar or non-polar).
- The strength of van der Waals forces decreases greatly as the distances between molecules increases.

Although van der Waals forces are weak compared to covalent or ionic bonds, they are present in large numbers. Therefore, **they play an important role in determining the physical properties of substances such as boiling points, melting points, and solubility**.

Intramolecular bonding is bonding that takes place within a molecule, i.e. the bond that holds the atoms together. Covalent bonding and polar covalent bonding are examples of intramolecular bonding.

Intermolecular forces are the forces of attraction that exist between molecules.

Figure 6.14 An intravenous injection is so called because the drug is being injected *inside* the vein. Intramolecular bonding is bonding that occurs *inside* the molecule, i.e. it holds the molecule together.

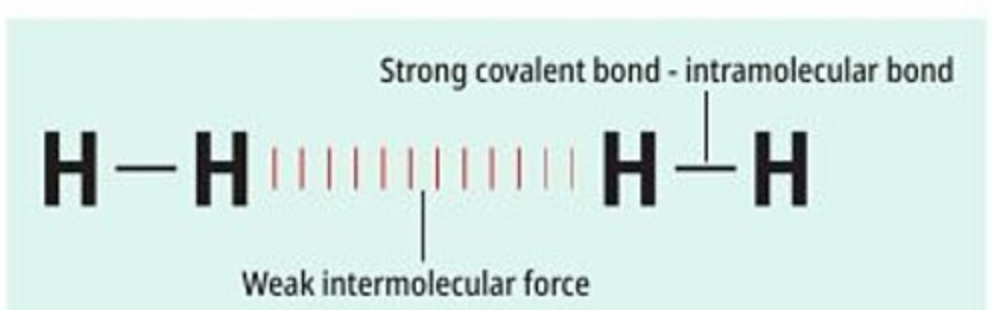
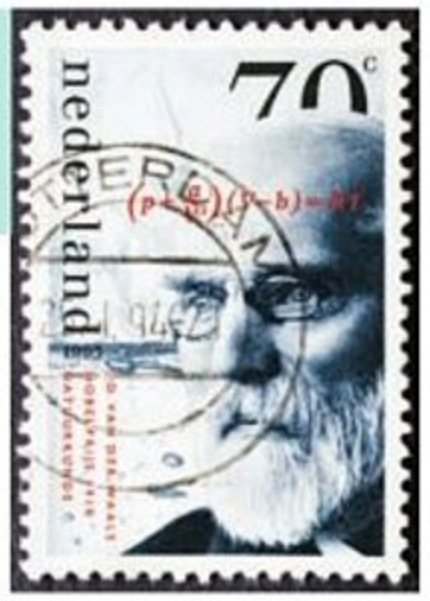


Figure 6.15 Intramolecular bonding is bonding **within** a molecule. Intermolecular forces are forces of attraction **between** molecules.

Figure 6.16 Johannes van der Waals discovered that there were weak attractive forces between molecules.



There are three main types of van der Waals forces which we will study on this course:

1. London dispersion forces.
2. Permanent dipole–dipole forces, including a special type of dipole–dipole force called hydrogen bonding.
3. Ion–dipole forces.

We will now discuss these types of intermolecular forces.

1. London dispersion forces

Imagine what happens to a molecule of hydrogen when another molecule of hydrogen comes near it, Figure 6.17.

Figure 6.17 London dispersion forces are weak attractive forces between temporary dipoles.

From our previous studies of bonding, we know that there are two electrons moving inside a molecule of hydrogen. As the two electrons move inside the molecule, it may happen that, at any one instant, both electrons may be closer to one end of the molecule than the other, i.e. one side of the molecule may be slightly negative leaving the other side of the molecule slightly positive.

- The picture may be compared to taking a series of random photographs. At a given instant in some photos, one part of the molecule may have slightly more electron density than another part. This means that a **temporary dipole** is set up in the molecule, i.e. two poles with one δ+ and the other δ−. It is temporary because it only exists for a short time. This is in contrast to the permanent dipole in a molecule of HCl. This temporary dipole is often called an **instantaneous dipole**, as it is only set up for a short time.
- This temporary dipole could cause a similar dipole to be set up in a nearby molecule. This process of setting up the dipole in a nearby molecule is called **induction**.
- There is then an attraction between the opposite charges as shown in Figure 6.17. This attraction is called a **London dispersion force** after the German-American scientist, Fritz London, who studied this particular type of van der Waals force in great detail, Figure 6.18. The word 'dispersion' refers to the fact that there is a temporary redistribution or dispersion of charge in the electron clouds. This temporary redistribution causes temporary dipoles to be set up.

London dispersion forces are weak forces of attraction between molecules resulting from the formation of temporary dipoles. They are the only forces of attraction between non-polar molecules.

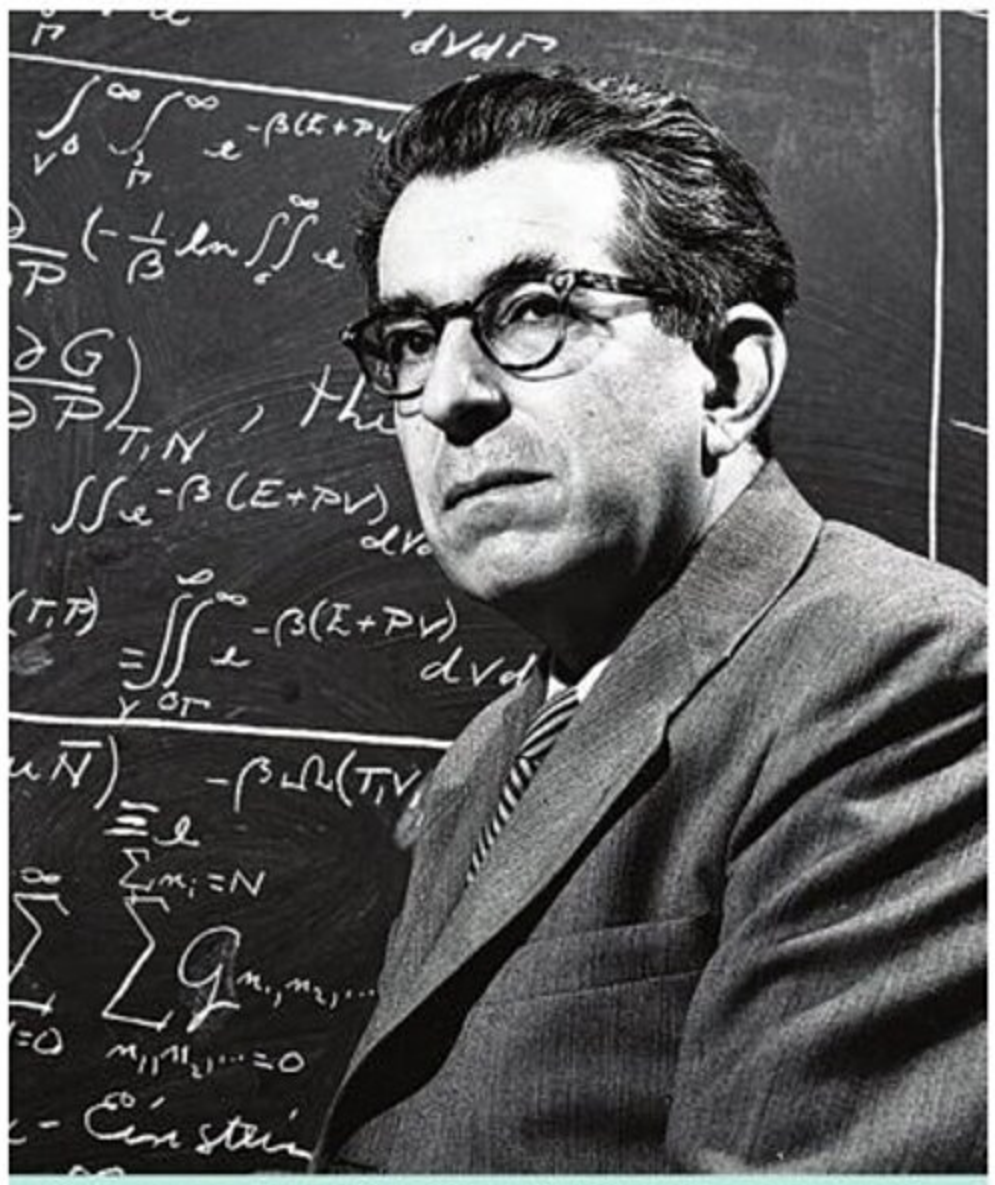


Figure 6.18 Fritz London studied the intermolecular forces between non-polar molecules.

- Since the electrons are moving about at high speed, the attraction between any two molecules only exists for an instant. These London dispersion forces are very weak. It has been estimated that this type of force is only about one-thousandth as strong as the covalent bond holding the atoms together in the molecule.
- London dispersion forces are the only forces of attraction that exist between non-polar molecules, e.g. H_2, O_2, N_2 and Cl_2.
- **London dispersion forces occur between all atoms and molecules, regardless of whether the molecule is polar or non-polar.** The reason for this is because electrons are in constant movement. As they move within the molecule, the motion leads to changes in the distribution of electron charge in the molecule. Therefore, at any given instant, the charge may be unevenly distributed. This gives rise to temporary dipoles as described above.
- London dispersion forces also exist between single atoms, e.g. the noble gases helium, neon and argon exist as single atoms, and London dispersion forces exist between all of the atoms. (Note that even though these elements exist as individual atoms, the London dispersion forces between the atoms are still referred to as 'intermolecular'.)

The effect of London dispersion forces on physical properties

- It has been found that the strength of London dispersion forces **increases as the molecules get larger in size**. This is because the increase in the number of electrons means bigger electron clouds, allowing the temporary dipoles to form more easily. The bigger atoms are said to have a higher **polarisability**. The greater the polarisability, the greater is the strength of the dispersion forces.
- For example, at room temperature, Cl_2 is a gas, Br_2 is a liquid and I_2 is a solid. This progression in boiling point is due to the increasing strength of the London dispersion forces. The strength of these forces increases because, as the relative molecular masses increase, the numbers of electrons increases, and the size of the electron clouds in the molecules increases. To convert a liquid to a gas, the particles of the liquid must be 'freed' from each other. Therefore, the forces of attraction between these particles must be broken. The boiling point reflects the energy required to overcome the intermolecular forces.

Study the data summarised in Table 6.2, as you could be given similar data in an exam and asked to explain the reason for the trend.

Molecule	Boiling point of element (°C)
F_2	−188
Cl_2	−34
Br_2	59
I_2	184

Table 6.2 Note the increase in boiling point as the size of the molecules increases. The increase in boiling point is due to the increasing strength of the London dispersion forces.

- Similarly, H_2 has a boiling point of –253 °C but O_2 does not boil until –183 °C. The higher boiling point of oxygen is due to the fact that the London dispersion forces in oxygen are stronger than in hydrogen, since the oxygen atom is bigger than the hydrogen atom, i.e. it contains more electrons than hydrogen and more temporary dipoles are formed. Therefore, more heat is required to break the stronger London dispersion forces formed between the bigger molecules of oxygen.
- London dispersion forces also exist in the case of the noble gases – all of which consist of atoms. The boiling points of these gases increase with the size of the atoms because of the increasing strength of the London dispersion forces, Figure 6.19. As you go down the group, the atoms increase in size and the greater number of electrons in the larger electron clouds allow the temporary dipoles to form more easily. (The boiling points are given on the Kelvin scale. We will study this scale in Chapter 9.)

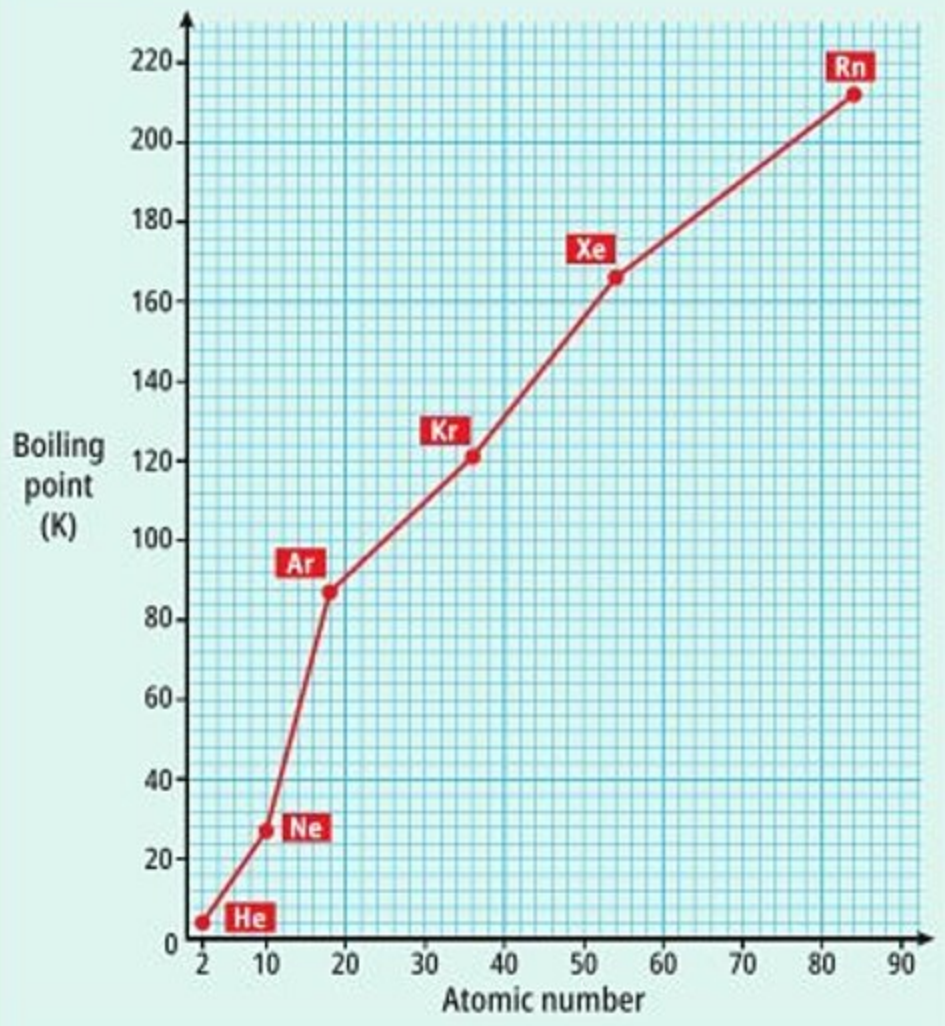


Figure 6.19 The boiling points of the noble gases increase with increasing atomic number because the strength of the London dispersion forces increases as the atoms get bigger.

- London dispersion forces are also used to explain the difference in the boiling points of compounds such as propane, C_3H_8 (–42 °C), and butane, C_4H_{10} (–1 °C). The molecules of both of these compounds are non-polar. Butane has a higher boiling point because it is a bigger molecule than propane and has more electrons and a bigger electron cloud than propane. Therefore, temporary dipoles are more easily formed in butane, causing greater numbers of London dispersion forces. Therefore, more heat must be supplied to boil butane than propane.
- London dispersion forces are used to explain why butane, C_4H_{10}, is a gas at room temperature but hexane, C_6H_{14}, is a liquid. The molecules of both of these compounds are non-polar. Hexane is a larger molecule with more electrons and a bigger electron cloud. Therefore, temporary dipoles are more easily formed, i.e. the London dispersion forces are strong enough to hold the molecules together as a liquid.
- London dispersion forces are used to explain why carbon dioxide is more easily liquefied than helium. Both gases are non-polar but the London dispersion forces are stronger in carbon dioxide than the London dispersion forces in helium because carbon dioxide is a larger molecule with more electrons and a bigger electron cloud. Therefore, temporary dipoles are more easily formed.

Example 6.2

Question

The boiling points of hydrogen and oxygen are 20.0 K and 90.2 K respectively.
Account for the higher boiling point of oxygen. [LCH]

Answer

Since both of these molecules are non-polar, the only intermolecular forces are London dispersion forces.

The strength of London dispersion forces increases as the molecules get bigger. Oxygen is a bigger molecule than hydrogen. Therefore, the London dispersion forces are stronger between oxygen molecules than between hydrogen molecules.

Therefore, it takes more energy to break the London dispersion forces in oxygen than in hydrogen, i.e. oxygen has a higher boiling point, Figure 6.20.

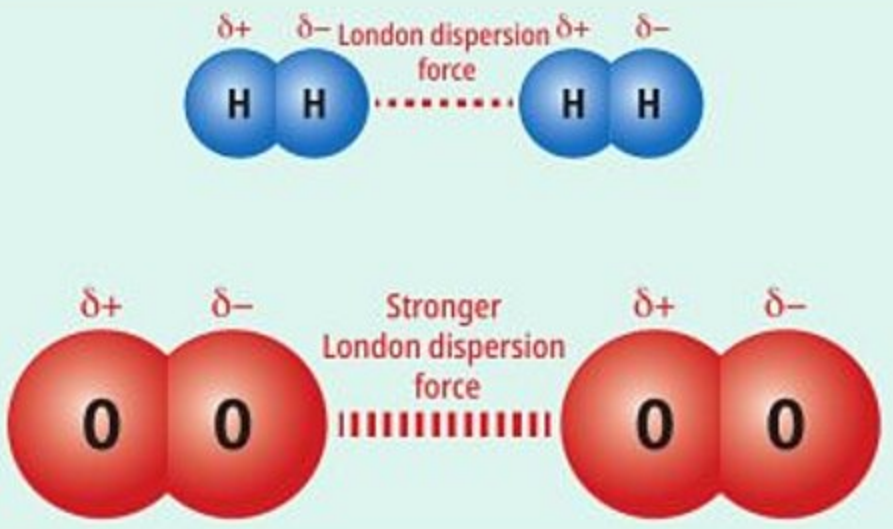


Figure 6.20 The boiling point of oxygen is higher than that of hydrogen because the London dispersion forces in oxygen are stronger than those in hydrogen. This is because the oxygen atom is bigger than the hydrogen atom and contains more electrons and a bigger electron cloud than hydrogen, i.e. more temporary dipoles are formed in the oxygen molecule than in the hydrogen molecule.

2. Dipole–dipole forces

In the previous section, we saw how temporary dipoles can lead to an attraction between one non-polar molecule and another. However, in compounds whose molecules are polar, forces called dipole-dipole forces exist permanently.

For example, since hydrogen chloride is a polar molecule, dipole–dipole forces exist between the molecules of HCl, Figure 6.21.

The main points about dipole–dipole forces may be summarised as follows:

- Dipole–dipole forces are caused by the partially negative end of one polar molecule attracting the partially positive end of a neighbouring polar molecule.
- Since dipole–dipole forces are between partial electric charges (δ– and δ+), these forces are much weaker than the ionic bonds holding ionic compounds together.
- Dipole–dipole forces only exist between molecules with a permanent dipole in the molecule. These forces are stronger than the temporary dipoles that cause London dispersion forces.
- Note in Figure 6.21 that the molecules align themselves so that oppositely charged ends of dipoles face each other – unlike charges attract each other.
- Similar to London dispersion forces, dipole–dipole forces decrease with increasing distance between the molecules.
- The dipole–dipole forces between the molecules give rise to higher boiling points than those of similar non-polar molecules. For example, the boiling point of HCl (–85 °C) is much higher than that of H_2 (–253 °C) as more heat must be supplied to overcome the greater strength of the dipole–dipole forces in HCl.
- Similarly, the boiling point of a substance called methanal (formaldehyde), HCHO, is much higher (–21 °C) than that of ethene, C_2H_4, (–104 °C). Dipole–dipole forces exist between the polar methanal (formaldehyde) molecules but only weaker London dispersion forces exist between ethene molecules since they are non-polar molecules, Figure 6.22.

Dipole–dipole forces are forces of attraction between the negative pole of one polar molecule and the positive pole of another polar molecule.

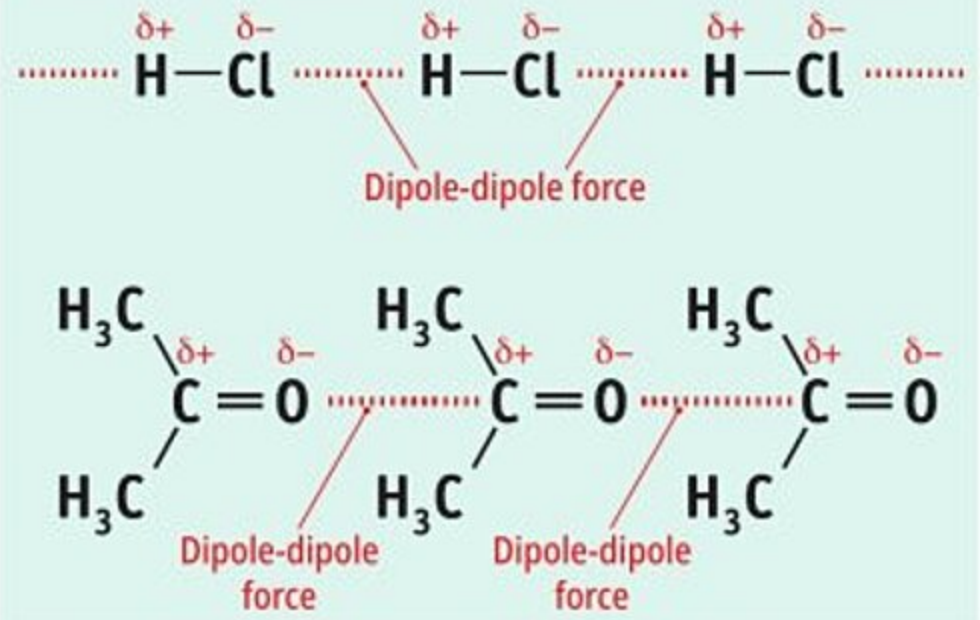


Figure 6.21 Dipole–dipole forces exist between polar molecules. Two examples are shown here: HCl and propanone (also called acetone), $(CH_3)_2CO$, used in nail varnish remover. For the sake of clarity, only three molecules are shown in the diagram. Remember that these forces act in all directions.

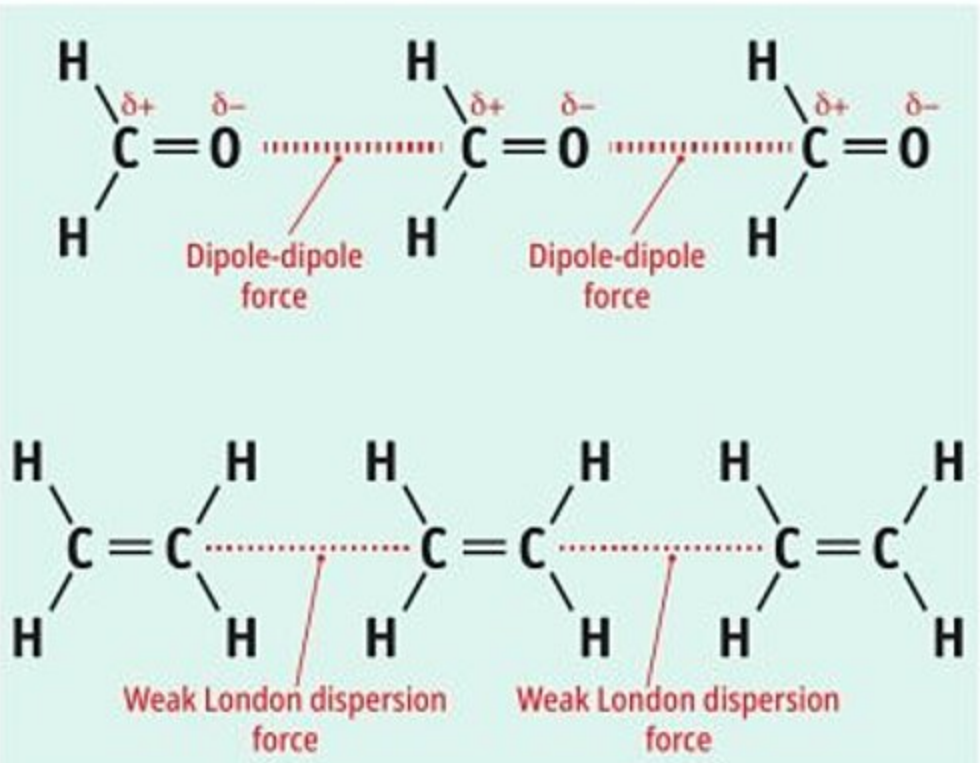


Figure 6.22 The dipole-dipole attractions between the molecules in methanal (formaldehyde) give it a much higher boiling point than that of ethene. There are no permanent dipole-dipole forces in ethene since it is a non-polar molecule. Only weak London dispersion forces exist between the ethene molecules.

» Study Example 6.3 in the online resources.

Hydrogen bonding: a special type of dipole–dipole force

When chemists studied the boiling points of water, ammonia and hydrogen fluoride, they found that the boiling points of these substances were far higher than expected. (These compounds are often referred to as hydrides, i.e. compounds of hydrogen and one other element.)

- H_2O has a boiling point of 100 °C but H_2S has a much lower boiling point of only –61 °C. Both oxygen and sulfur are in the same group of the Periodic Table. Why the big difference in boiling points?
- Similarly NH_3 has a boiling point of –33 °C but PH_3 has a far lower boiling point of only –88 °C.
- Finally, HF has a boiling point of 20 °C but HCl has a boiling point of only –85 °C.
- The fact that the boiling points of water, ammonia and hydrogen fluoride are remarkably high is very obvious when one studies the boiling points of various hydrides, Figure 6.24.
- Note the bottom line (Group IV or 14) where the boiling points of the compounds CH_4, SiH_4, GeH_4 and SnH_4 increase regularly. The reason for this is because these molecules only have intermolecular forces that consist of weak London dispersion forces. This regular increase is what we expect because London dispersion forces increase as the number of electrons increase with the increasing size of each molecule. We might expect this regular increase to be repeated in the other three series shown in the graph.
- However, it is clear in Figure 6.24 that the regular increase is not observed for the nitrogen group (Group V or 15), the oxygen group (Group VI or 16) or the fluorine group (Group VII or 17).
- Therefore, the molecules of H_2O, NH_3 and HF must have stronger intermolecular forces pulling them together than if there were just London dispersion or simple dipole–dipole forces present as discussed in the previous section. This type of strong dipole–dipole attraction is given the special name of **hydrogen bond**.

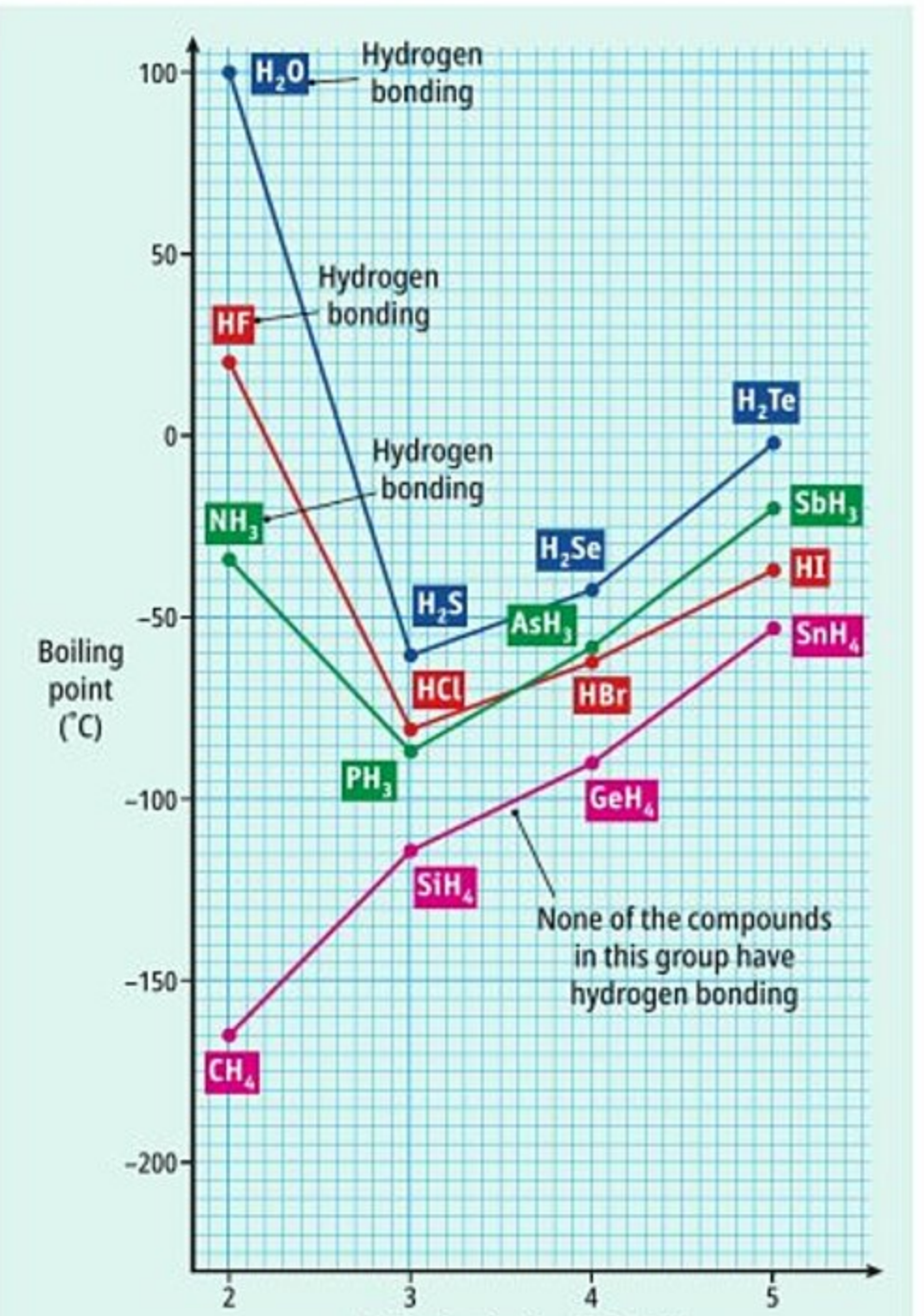


Figure 6.24 The high boiling points of H_2O, HF and NH_3 are evidence for the existence of hydrogen bonding in these three compounds. Note how much higher the boiling points of these compounds are compared with the boiling points of the hydrogen compounds of the other elements in the same group.

The main points about hydrogen bonding are:

- Hydrogen bonding arises when an atom of hydrogen is bonded to an atom of **fluorine or oxygen or nitrogen**, i.e. with the three most electronegative elements in the Periodic Table. The hydrogen bonds in the compounds HF, H_2O and NH_3 are shown in Figure 6.25.

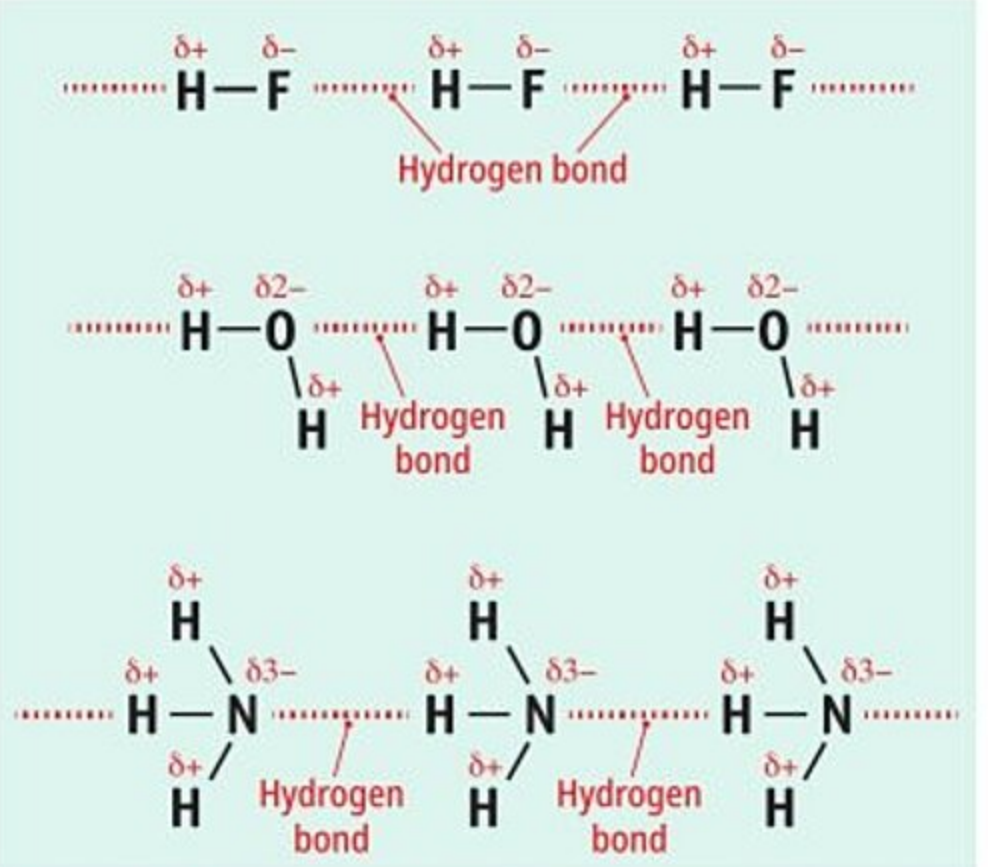

δ+ δ− δ+ δ− δ+ δ−
H—F H—F H—F
Hydrogen bond
δ+ δ2− δ+ δ2− δ+ δ2−
H—O H—O H—O
δ+ δ+ δ+
H Hydrogen bond H Hydrogen bond H
δ+ δ+ δ+
H H H
δ+ δ3− δ+ δ3− δ+ δ3−
H—N H—N H—N
δ+ δ+ δ+
H Hydrogen bond H Hydrogen bond H

Figure 6.25 Hydrogen bonding occurs in hydrogen fluoride, water and ammonia.

- As is the case with other intermolecular forces, hydrogen bonds are shown by dashed lines. Note from Figure 6.25 that the hydrogen atoms form a sort of 'bridge' between the two molecules, i.e. the hydrogen atom is bonded to one atom by a covalent bond and to the other atom by a hydrogen bond.
- The hydrogen atom in each of the three compounds H_2O, HF and NH_3 has a fairly strong partial positive charge because, in each case, it is bonded to a very electronegative element. This causes a strong polarity in the molecules and they line up in molecular chains or groups that hold the molecules together quite strongly. (To help you remember the three elements – nitrogen, oxygen and fluorine – involved in hydrogen bonding, think of 'NOF'.)
- The high boiling points in H_2O, NH_3 and HF are caused by the fact that considerable energy must be supplied to break the hydrogen bonds so that the molecules can be separated from each other and escape from the liquid.
- Hydrogen bonds are much stronger than either London dispersion forces or dipole–dipole forces. However, they are much weaker than ordinary covalent bonds. It has been calculated that the strength of a hydrogen bond is about 10% of that of a covalent bond.
- Despite the fact that hydrogen bonds are much weaker than covalent bonds, the effect of hydrogen bonding is significant because so many hydrogen bonds are present.

Hydrogen bonds are formed by a particular type of dipole–dipole attractions between molecules in which hydrogen atoms are bonded to nitrogen, oxygen or fluorine. The hydrogen atom carries a partial positive charge and is attracted to the electronegative atom in another molecule. Thus, the hydrogen bond acts as a bridge between two electronegative atoms in separate molecules.

- Note in Figure 6.24 that the boiling point of H_2O (100 °C) is higher than that of NH_3 (–33 °C). The reason for this is because **the electronegativity of oxygen is higher than that of nitrogen**. Therefore the hydrogen bonding in H_2O is stronger than that in NH_3, since the O–H bond is more polar than the N–H bond. Therefore, more energy is required to break the hydrogen bonds in H_2O and to separate the molecules of H_2O from each other so that they can escape from the liquid.
- Note in Figure 6.25 that the boiling point of H_2O (100 °C) is higher than that of HF (19.5 °C). This is because there are **twice as many hydrogen bonds for each molecule of H_2O than there are for each molecule of HF** – even though the individual hydrogen bonds between HF molecules are stronger, as fluorine is more electronegative than oxygen. Therefore, it takes more energy to break the hydrogen bonds in H_2O and to separate the molecules of H_2O from each other so that they can escape from the liquid.
- The strength of hydrogen bonds is approximately ten times as strong as other dipole–dipole forces. It is only about ten times weaker than a covalent bond.

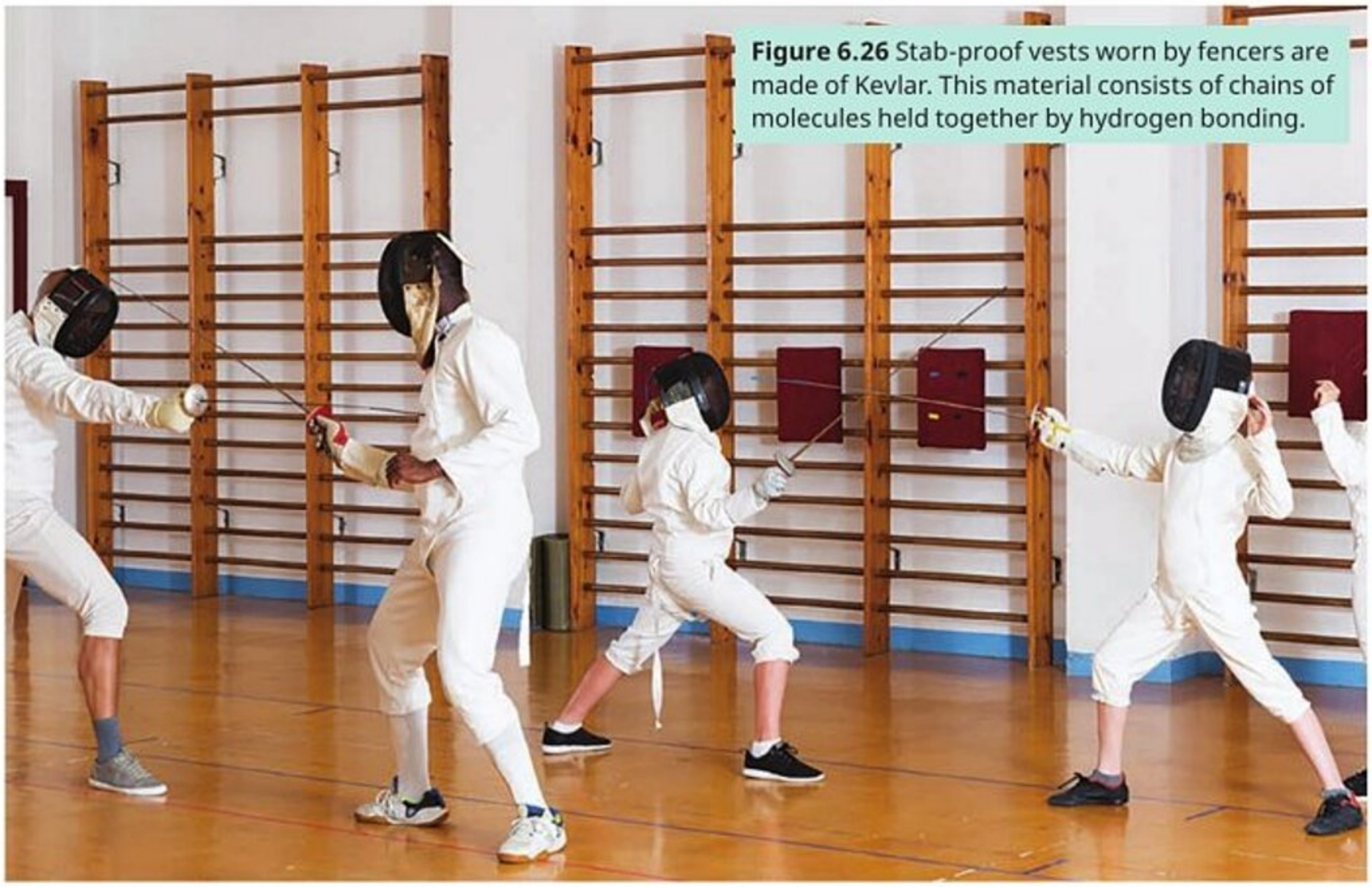


Figure 6.26 Stab-proof vests worn by fencers are made of Kevlar. This material consists of chains of molecules held together by hydrogen bonding.

Hydrogen bonding is very important in our everyday lives. If hydrogen bonding did not exist in water, then water would be a gas at room temperature and life, as we know it, could not exist on Earth. Hydrogen bonding is also very important in synthetic clothing. Kevlar is a type of fibre developed by the DuPont company, Figure 6.26. It is fire-resistant, extremely strong and flexible. Kevlar is strong because long chains of molecules line up parallel to each other and are held together strongly by hydrogen bonding. This makes Kevlar an ideal material for making bullet-proof vests, jackets for fencers and protective suits for professional motorcyclists.

Hydrogen bonding also helps fibres absorb water. Wool contains chains of substances called proteins that contain many oxygen and nitrogen atoms. These atoms can form hydrogen bonds with water. This means that wool can absorb water and does not feel clammy to wear.

Hydrogen bonding explains many of the properties of water:

- **Boiling and melting points:** Water has a much higher boiling point (100 °C) and melting point (0 °C) than other molecules of similar size, such as methane (CH_4). This is because extra energy is needed to overcome the hydrogen bonding.
- **Excellent solvent:** The polarity of water molecules, combined with hydrogen bonding, allows water to dissolve ionic compounds (such as salt) and polar molecules (such as HCl). Water is often called the 'universal solvent' because so many substances dissolve in it. We will discuss this in more detail later.
- **High surface tension:** At the surface of water, hydrogen bonds pull the water molecules together. This effect is known as surface tension and it forms a type of 'skin' on water. This allows some insects to walk on its surface.

Example 6.4

Question

Use your knowledge of intermolecular forces to explain why methane has a very low boiling point (bp = –164 °C).

The relative molecular mass of methane is only slightly lower than that of water but the boiling point of water is much higher (bp = 100 °C). Suggest a reason for this.

[LCH]

Answer

Methane is non-polar and so the forces of attraction that exist between its molecules are weak London dispersion forces. Therefore, little energy is needed to separate methane molecules from each other, i.e. methane has a low boiling point.

Water is a polar molecule and hydrogen bonds exist between its molecules. The boiling point of water is much higher than that of methane because of the much stronger hydrogen bonds between the water molecules. Hydrogen bonding does not exist in methane.

Solubility in water and hydrogen bonding

Since water is a polar covalent solvent, many compounds which are also polar covalent tend to dissolve in it ('like dissolves like'). Ammonia is an example of a polar covalent compound that is extremely soluble in water. The high solubility of ammonia in water may be shown by the 'Fountain Experiment', Figure 6.27.

The reason for the high solubility of ammonia in water may be understood by studying what happens when ammonia dissolves in water, Figure 6.28.

- Note the formation of hydrogen bonds between the slightly negative nitrogen atoms ($N^{\delta 3-}$) of ammonia with the slightly positive hydrogen atoms ($H^{\delta +}$) of water.
- Note the formation of hydrogen bonds between the slightly positive hydrogen atoms ($H^{\delta +}$) of ammonia and the slightly negative oxygen atoms ($O^{\delta 2-}$) of water.

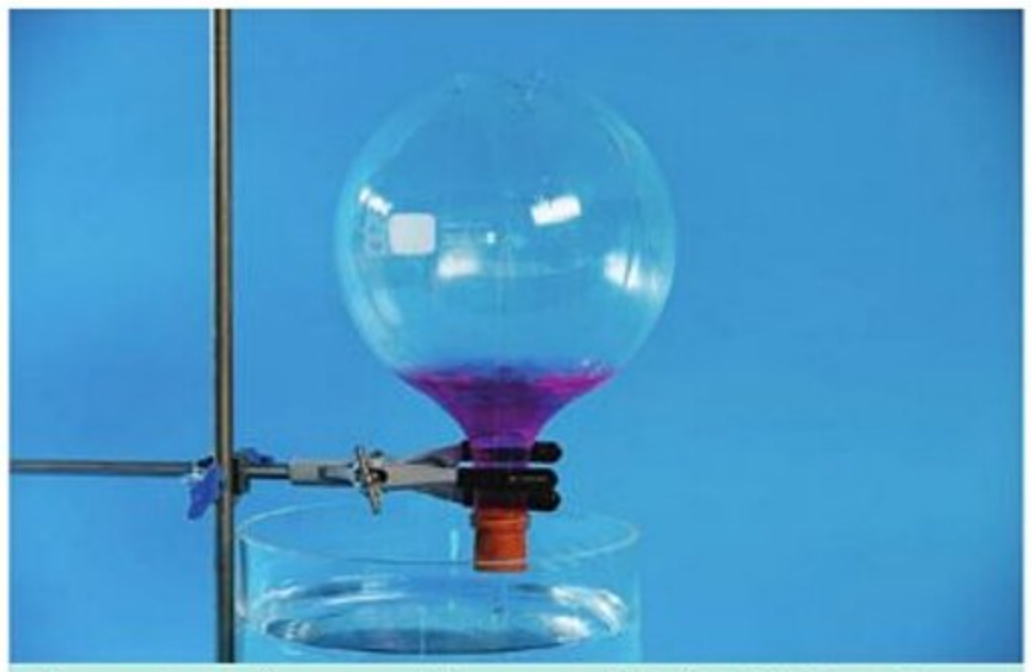


Figure 6.27 The round-bottomed flask is filled with ammonia gas. As soon as water enters the flask, the first drop of water dissolves the entire flask of ammonia. This causes a fall in pressure inside the flask and the water 'fountains' into the flask. Some phenolphthalein has been added to the water so that it turns pink when it comes in contact with the ammonia.

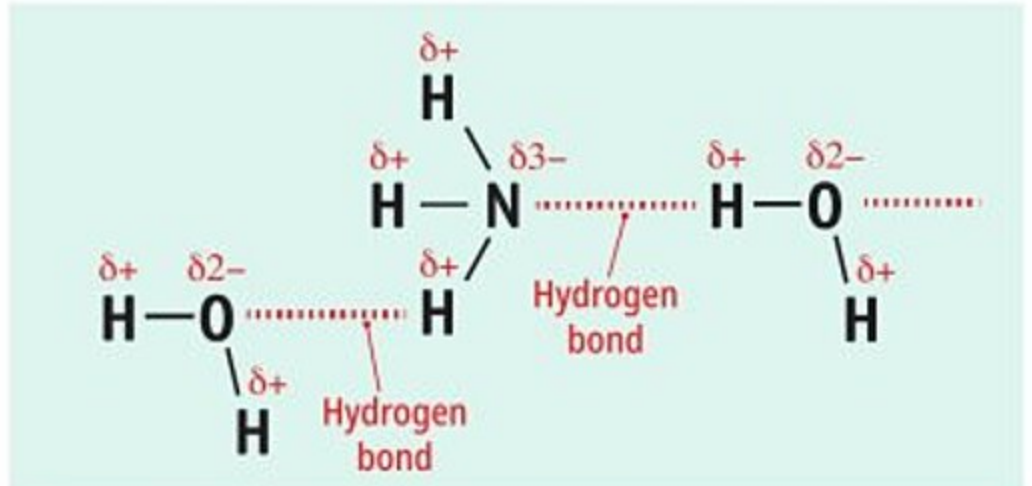


Figure 6.28 NH_3 is very soluble in water, as hydrogen bonds are formed between the slightly negative N atoms ($N^{\delta 3-}$) of NH_3 and the slightly positive H atoms ($H^{\delta +}$) of H_2O, and also between the slightly positive hydrogen atoms of NH_3 ($H^{\delta +}$) and the slightly negative O atoms ($O^{\delta 2-}$) of H_2O, as shown in the diagram. For clarity, only two hydrogen bonds are shown.

In short, ammonia is very soluble in water due to the fact that the ammonia molecule forms hydrogen bonds with the water molecule. This helps the ammonia to form a perfect mixture with the water, i.e. it readily dissolves.

- The general rule 'like dissolves like' summarises a lot about solubility.
- Polar substances such as HCl readily dissolve in a polar solvent such as water.
- In the case of ammonia, even if we knew nothing about hydrogen bonding, we would expect it to dissolve in water, since it is a polar substance.
- Non-polar substances such as methane, oil and most plastics do not dissolve in water. This is because non-polar substances have no charged ions or partially charged molecules. Therefore, the positive and negative ends of the water molecules are not attracted to these molecules. Therefore, oil and water do not mix.
- Similarly, iodine crystals (non-polar) will not dissolve in water, Figure 6.29, but will dissolve in a non-polar solvent such as hexane (C_6H_{14}). This is due to the existence of London dispersion forces between the molecules of the iodine and those of the hexane.
- A gas called phosphine, PH_3, is virtually insoluble in water since phosphine is non-polar (electronegativity values of P and H = 2.19 and 2.20 respectively – almost identical). However, it will dissolve in hexane due to the existence of London dispersion forces between the molecules of the phosphine and those of the hexane.

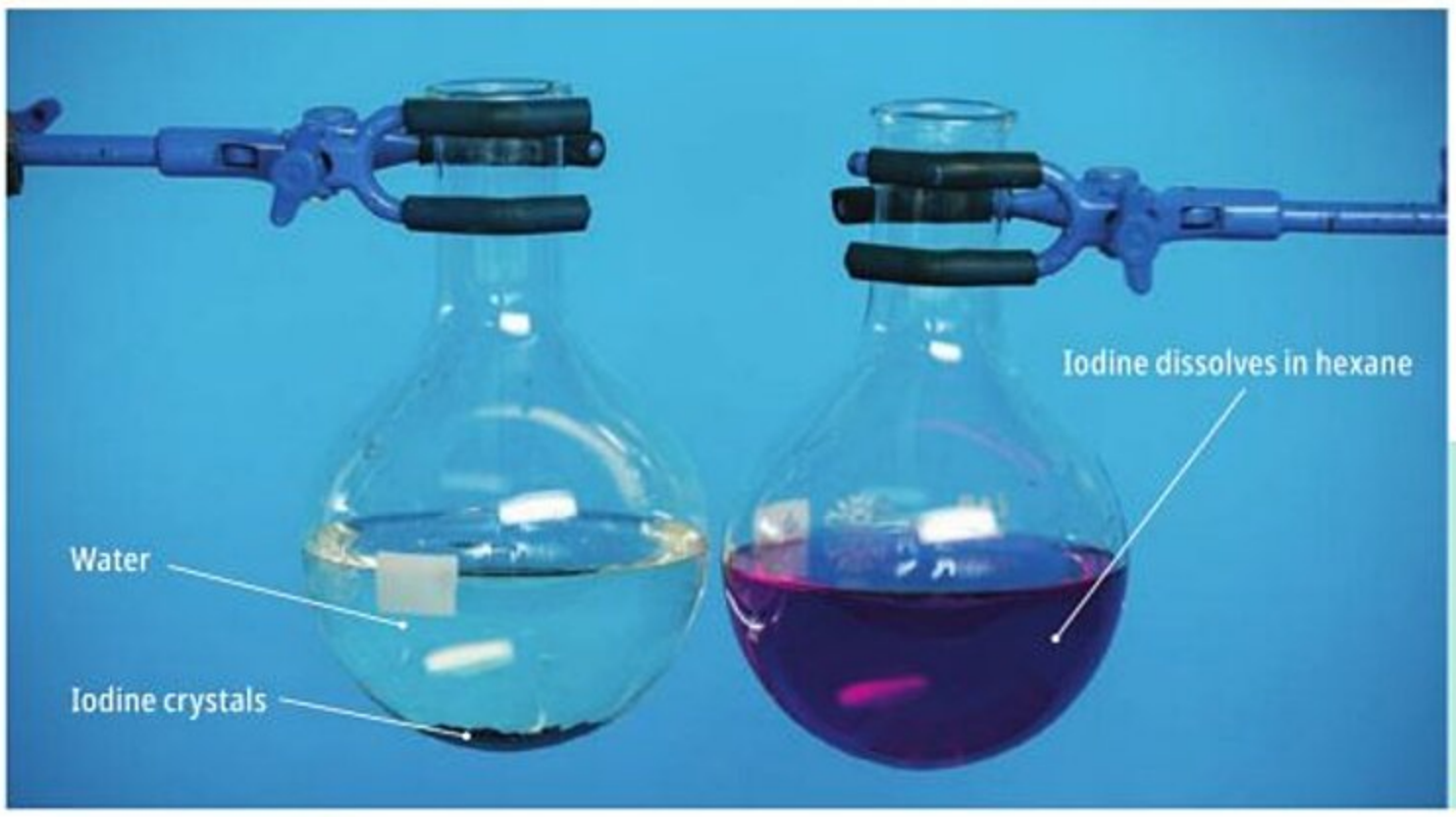


Figure 6.29 'Like dissolves like.' Iodine is non-polar. Therefore, iodine crystals do not dissolve in water (polar) but will dissolve in hexane (non-polar).

Example 6.5

Question

Hydrogen sulfide has a boiling point of 212.3 K and water has a boiling point of 373 K. Account for the difference in the boiling points of these substances.

[LCH]

Answer

Hydrogen bonding exists in water as there is a large electronegativity difference (1.24) between O and H. Hydrogen bonding does not exist in H_2S, as the electronegativity difference between S and H is smaller (0.38) than between O and H. Therefore, the dipole–dipole intermolecular forces in H_2S are weaker than the hydrogen bonding intermolecular forces in H_2O. Therefore, H_2S has a lower boiling point than water.

3. Ion–dipole forces

One of the most important properties of water is the fact that it is an excellent solvent. This property depends on the fact that water is a polar molecule. It is found that most ionic substances and most polar-covalent substances dissolve in water. An ionic substance such as sodium chloride dissolves in water because the ionic bonding in NaCl is overcome by the strong attraction between the ions and the polar water molecules, Figure 6.30. These ions are dragged away from the crystal lattice and become surrounded by water molecules i.e. the salt dissolves.

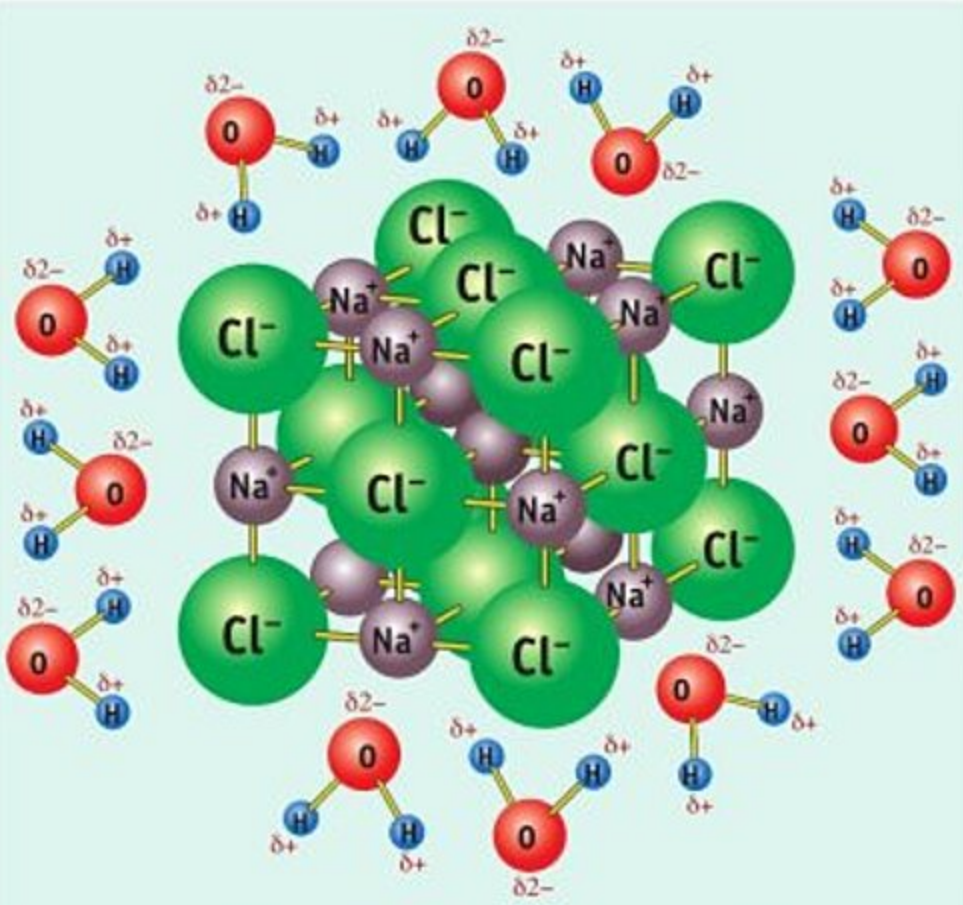


Figure 6.30 Sodium chloride dissolves readily in water. Note how the polar water molecules line up around the ions and draw them into solution.

An **ion–dipole force** is the force of attraction between an ion and a polar molecule.

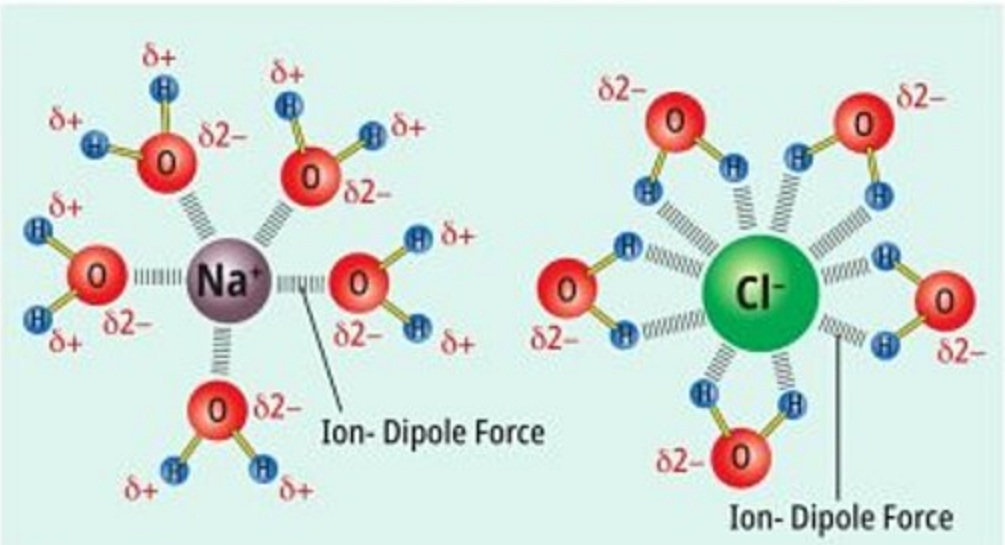


Figure 6.31 Ion–dipole forces exist between (a) positive ions and the negative pole of the water molecules, and (b) between negative ions and the positive poles of the water molecule.

Note from Figure 6.30 that the negative end of the water molecule is attracted to the positive sodium ion. Also, the positive end of the water molecule is attracted to the negative chloride ion. This is true of all ion–dipole forces.

These ion–dipole forces are shown in Figure 6.31.

Evidence for existence of intermolecular forces

We have now concluded our study of all the intermolecular forces on our course. The following points summarise some evidence that intermolecular forces exist:

1. Trends in physical properties can only be explained if intermolecular forces are present.
2. In many cases, experimental evidence can only be explained by the presence of intermolecular forces. For example, non-polar gases such as hydrogen, oxygen, nitrogen, helium and neon, can condense into liquids at low temperature. This demonstrates that there are weak attractive forces between the atoms or molecules holding them in the liquid state.
3. Some non-polar substances such as iodine exist as solids at room temperature. The solid state implies that the intermolecular forces are strong enough to hold the molecules together in a crystal lattice.
4. Calculations involving the behaviour of very small particles such as electrons (i.e. quantum mechanics) predict the presence of intermolecular forces.

6.5 Physical properties of ionic and covalent compounds

We have seen that ionic compounds usually consist of a network of ions, whereas covalent compounds generally consist of individual molecules. Many of the properties of ionic and covalent compounds can be understood if we keep these facts in mind. These properties are summarised in Figure 6.32.

(a) State of matter at room temperature

- Most **ionic** compounds are solid at room temperature. This is because they consist of crystal lattice structures. The strong forces of attraction between the oppositely charged ions mean that a lot of energy would be required to break the bonds. Therefore, they are solid at room temperature.
  - Examples: Sodium chloride (NaCl) and limestone ($CaCO_3$) are solid at room temperature.
- Most **covalent** substances are either liquids or gases at room temperature. This is because the forces between one molecule and another are weaker than those found in ionic compounds.
  - Examples: Oxygen (O_2) and carbon dioxide (CO_2) are gases and water (H_2O) is a liquid.

(b) Melting and boiling points

- In **ionic** compounds, the ions can only vibrate about fixed positions. When heat is supplied, the ions gain energy and vibrate more and more. Eventually, the ions vibrate so much that they break away from their fixed positions in the crystal. When this happens, the crystal structure breaks down and we observe the substance melting. However, because the forces of attraction between the ions are so strong, most ionic substances have high melting points and high boiling points.
  - Example: The melting point of sodium chloride is 801 °C and its boiling point is 1413 °C.
- In **covalent** substances, there are only weak forces between the molecules. Therefore, the melting points and boiling points are much lower than ionic compounds.
  - Example: The melting point of iodine is 114 °C and its boiling point is 184 °C.

Other covalent substances have even lower melting and boiling points, e.g. water (m.p. = 0 °C, b.p. = 100 °C), ammonia (m.p. = –77 °C, b.p. = –33 °C), methane (m.p. = –182 °C, b.p. = –164 °C). Therefore, as mentioned above, at room temperature, most covalent compounds are usually either liquids or gases.

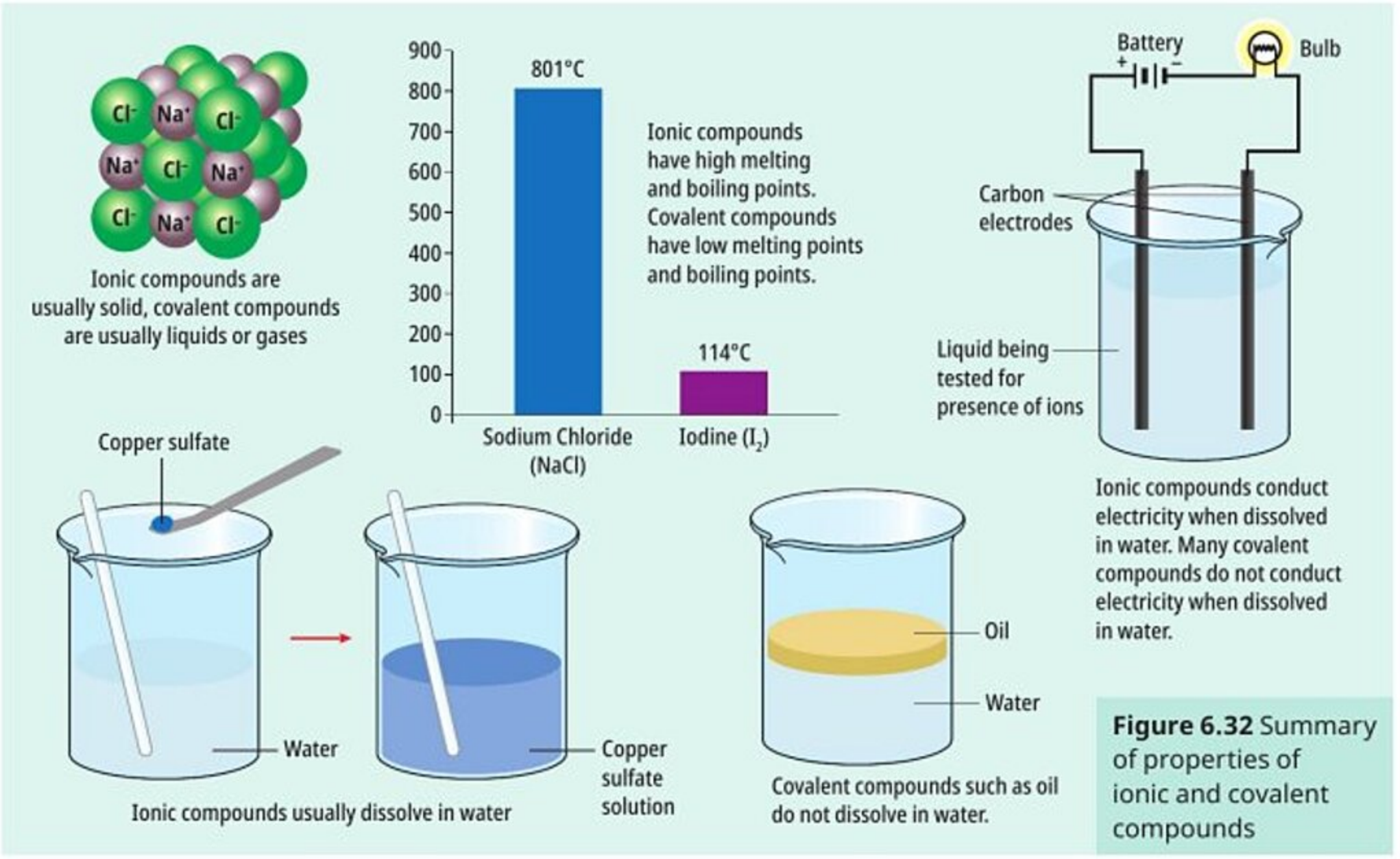


Figure 6.32 Summary of properties of ionic and covalent compounds

(c) Electrical conductivity

- Ionic compounds do not conduct electricity in the solid state. The reason for this is because the ions are locked in fixed positions and cannot carry the electric current through the crystal. However, if the ionic substance is **melted** or **dissolved in water**, the ions are now free to move. The electricity can now pass through the solution or molten salt as the ions carry the current. Therefore, molten ionic compounds and ionic compounds in solution conduct an electric current. The fact that the bulb lights (Figure 6.32) indicates that there are ions in solution. It does not necessarily mean that the substance that was originally dissolved in the water is ionic. For example: Hydrogen chloride is a covalent substance that dissolves in water to give ions:

$$HCl \rightarrow H^+ + Cl^-$$

- Covalent compounds do not usually conduct electricity. The reason for this is because they do not contain ions to carry the electric current.

(d) Solubility in water

Ionic compounds are usually soluble in water. The ions in ionic compounds are attracted to the polar water molecules through ion–dipole interactions. The water molecules surround the ions and dissolve the compound.

The solubility of covalent compounds depends on whether the molecules are polar or non-polar. Polar covalent compounds such as HCl and NH_3 are highly soluble in water due to dipole–dipole interactions. However, non-polar covalent substances such as O_2 and CH_4 are only sparingly soluble in water. For example, only 9.2 mg of oxygen will dissolve in a litre of water at 20 °C. However, the fact that a small amount of oxygen dissolves is very important for the survival of fish. Some compounds such as oils and fats are classified as insoluble in water.

- Covalent compounds do not usually conduct electricity as solids, liquids or gases, or when dissolved in water. The reason for this is because covalent substances do not contain ions to carry the electric current. The properties of ionic and covalent compounds are summarised in Table 6.3.

Ionic	Covalent
Contain a network of ions in the crystal	Contain individual molecules
Usually hard and brittle	Usually soft
Have high melting points and boiling points	Have low melting and boiling points
Usually solid at room temperature	Usually liquids, gases or soft solids at room temperature
Conduct electricity in molten state or when dissolved in water	Do not conduct electricity
Usually soluble in water	Solubility depends if polar covalent (soluble) or Non-polar (insoluble or sparingly soluble)

Table 6.3 The properties of ionic and covalent substances.

TEST YOURSELF: Attempt Questions 6.2 and W6.3–W6.13.

Summary What I should know

- **Electronegativity** is the relative attraction that an atom in a molecule has for the shared pair of electrons in a covalent bond.
- A **polar covalent bond** is a bond in which there is unequal sharing of the pair of electrons. This causes one end of the bond to be slightly positive (δ+) and the other end to be slightly negative (δ-).
- **Electronegativity values** may be used to predict the polarity of covalent bonds and also to predict which compounds are ionic and which are covalent.
- **A polar molecule** is a molecule that has an uneven distribution of electrical charges. This means that the molecule has regions (poles) with partial positive and partial negative charges separated by a distance.
- **A non-polar molecule** is a molecule that has an even distribution of electrical charges. This means that the molecule has regions (poles) with partial positive and partial negative charges that are not separated by a distance but coincide with each other.
- **Intermolecular forces** are the forces of attraction that exist between molecules. Examples of intermolecular forces are London dispersion forces, dipole–dipole forces, hydrogen bonding and ion–dipole forces.
- **Van der Waals forces** are weak, intermolecular forces of attraction that exist between all molecules.
- **London dispersion forces** are weak forces of attraction between molecules resulting from the formation of temporary dipoles. They are the only forces of attraction between non-polar molecules.
- **Dipole–dipole forces** are forces of attraction between the negative pole of one polar molecule and the positive pole of another polar molecule.
- **Hydrogen bonds** are particular types of dipole–dipole attractions between molecules in which hydrogen atoms are bonded to nitrogen, oxygen or fluorine.
- **An ion–dipole force** is the force of attraction between an ion and a polar molecule.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the concept of electronegativity.	⬡	⬡	⬡
Describe the nature of chemical bonds that lie on a continuum from ionic, through polar covalent, to pure covalent bonds.	⬡	⬡	⬡
Distinguish between intramolecular bonding and intermolecular forces.	⬡	⬡	⬡
Explain van der Waal's forces, London dispersion forces, permanent dipole–dipole forces, hydrogen bonding and ion–dipole forces.	⬡	⬡	⬡
Discuss how intermolecular forces can influence physical properties of various substances.	⬡	⬡	⬡

Chapter review questions

6.1

(a) Explain the term *electronegativity*.

(b) You are supplied with a table of electronegativity values for the Leaving Certificate exam. Give one use for this table.

(c) Distinguish between a polar covalent bond and a pure covalent bond.

(d) Give two examples of molecules that are polar covalent and two examples of molecules that are pure covalent.

(e) What is meant by the term *polar molecule*?

(f) Give two examples of polar molecules.

(g) Carbon dioxide has two polar bonds but it is a non-polar molecule. Explain.

6.2 Answer the following questions by referring to the first 36 elements of the Periodic and to the table of electronegativity values.

(a) Name one non-metal which exists as single atoms. [LCH]

(b) Give the formula of an ionic compound formed by an element in Group II and show the charge on each ion. [LCH]

(c) Give the formula of a covalent compound formed by an element in Group V and show clearly the electron structure of the molecule. [LCH]

(d) Comment on the nature of the bonds you would expect to find in each of the compounds MgS and PH_3. [LCH]

(e) Which two of the first 36 elements would form the compound you would expect to have the greatest ionic character? [LCH]

(f) What causes a temporary dipole to form in a hydrogen molecule?

(g) What is the term for the process by which a temporary dipole induces a dipole in a nearby molecule?

(h) What type of molecules experience only London dispersion forces as their intermolecular force?

(i) Why are London dispersion forces present in all atoms and molecules?

(j) What property increases in atoms and molecules to result in stronger London dispersion forces?

(k) What type of molecules experience dipole-dipole forces?

(l) What causes dipole–dipole forces to form between molecules?

(m) How do dipole–dipole forces compare in strength to London dispersion forces?

(n) What effect do dipole–dipole forces have on the boiling points of substances?

(o) What type of intermolecular force explains the unexpectedly high boiling points of water, ammonia, and hydrogen fluoride?

(p) Which three elements must hydrogen be bonded to in order for hydrogen bonding to occur?

(q) Why is the boiling point of H_2O much higher than that of H_2S, even though both oxygen and sulfur are in the same group?

(r) Why does hydrogen bonding result in stronger intermolecular attraction than ordinary dipole–dipole forces?

(s) What is the approximate strength of a hydrogen bond compared to a covalent bond?

(t) Why is the boiling point of water higher than that of ammonia?

(u) Why does water have a higher boiling point than HF, even though fluorine is more electronegative than oxygen?

(v) How does hydrogen bonding contribute to water's high surface tension?

7 Families and Trends in the Periodic Table

OBJECTIVES

- To make students familiar with trends in atomic radius, ionisation energy and electronegativity in the Periodic Table.
- To give students an understanding of the properties of Group 1 (Alkali Metals), Group 2 (Alkaline Earth Metals), Group 17 (Halogens) and Group 18 (Noble Gases) of the Periodic Table.
- To ensure that students know how to explain and predict properties of the elements in Groups 1, 2, 17 and 18, using their knowledge of the above trends.

7.1 Introduction

In Chapter 4, we studied the development and overall structure of the modern Periodic Table. We learned that when elements are arranged in order of increasing atomic number, the properties of the elements recur periodically. In other words, the properties displayed by an element are repeated in other elements within the same group or family in the Periodic Table. In this chapter, we will begin by studying some general trends in the Periodic Table and then focus on four specific groups (families) of elements. We will discuss how properties of the elements repeat within each group of elements. We will then discuss how the trends in repetition of properties may be explained and predicted using our knowledge of general trends in the Periodic Table.

7.2 Trends in atomic radii

You might think that the atomic radius of an atom is the distance from the nucleus of the atom to the outermost electrons. However, since the position of an electron cannot be precisely located (Heisenberg Uncertainty Principle), it is not possible for chemists to measure exactly where the electron cloud of an atom ends. It is possible, however, for chemists to measure experimentally the distance between the nuclei of atoms, Figure 7.1. This distance is known as the **bond length** and may be measured by methods known as 'X-ray diffraction' and 'electron diffraction'.

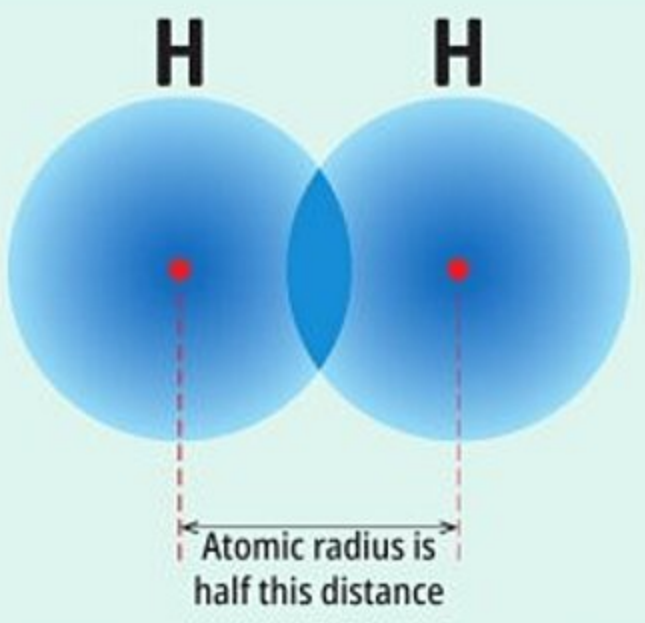


Figure 7.1 The atomic radius (covalent radius) is half the distance between the nuclei of two atoms of the same element that are joined together by a single covalent bond.

This atomic radius is also called the **covalent radius** and is defined as follows:

The **atomic radius (covalent radius)** of an atom is defined as half the distance between the nuclei of two atoms of the same element that are joined together by a single covalent bond.

For example, in a molecule of hydrogen it is found that the distance between the two nuclei is 0.074 nanometres (1 nm = 1×10^{-9} m).

Therefore, the covalent radius of a hydrogen atom is $\frac{0.074}{2} = 0.037$ nm.

Similarly, in a molecule of chlorine it is found experimentally that the distance between the two nuclei is 0.198 nm. Therefore the covalent radius of a chlorine atom is 0.099 nm.

A list of atomic radii (covalent radii) is given in Figure 7.2. Note that no values of covalent radii are quoted for the noble gases in Figure 7.2. This is because these elements exist as single atoms – they do not form covalent bonds with one another.

H 0.037																	He --
Li 0.123	Be 0.089											B 0.080	C 0.077	N 0.074	O 0.074	F 0.072	Ne --
Na 0.157	Mg 0.136											Al 0.125	Si 0.117	P 0.110	S 0.104	Cl 0.099	Ar --
K 0.203	Ca 0.174	Sc 0.144	Ti 0.132	V 0.122	Cr 0.117	Mn 0.117	Fe 0.116	Co 0.116	Ni 0.115	Cu 0.117	Zn 0.125	Ga 0.125	Ge 0.122	As 0.121	Se 0.117	Br 0.114	Kr --

Figure 7.2 The atomic radii (covalent radii) in nanometres of some elements.

If we examine the values of atomic radii in Figure 7.2, a definite pattern or trend emerges. To help you to see the trend, the values of atomic radii for the first 35 elements are plotted in Figure 7.3.

In general, the values of the atomic radii decrease along a period and increase down a group. This is shown in Figure 7.4.

- One of the factors that determines the size of an atom is the number of orbits (energy levels) that contain electrons. For example, an atom with its outermost electrons in the third orbit will be larger than one with its outermost electrons in the second orbit.
- The size of an atom is also influenced by the electrostatic attraction between the positively charged protons in the nucleus and the negatively charged electrons in the orbits.
- If this attraction is large, the positive protons will pull the outer electrons closer to the nucleus giving a smaller atomic radius.
- If the attraction is small, the electrons will be found further from the nucleus, giving a larger atomic radius.

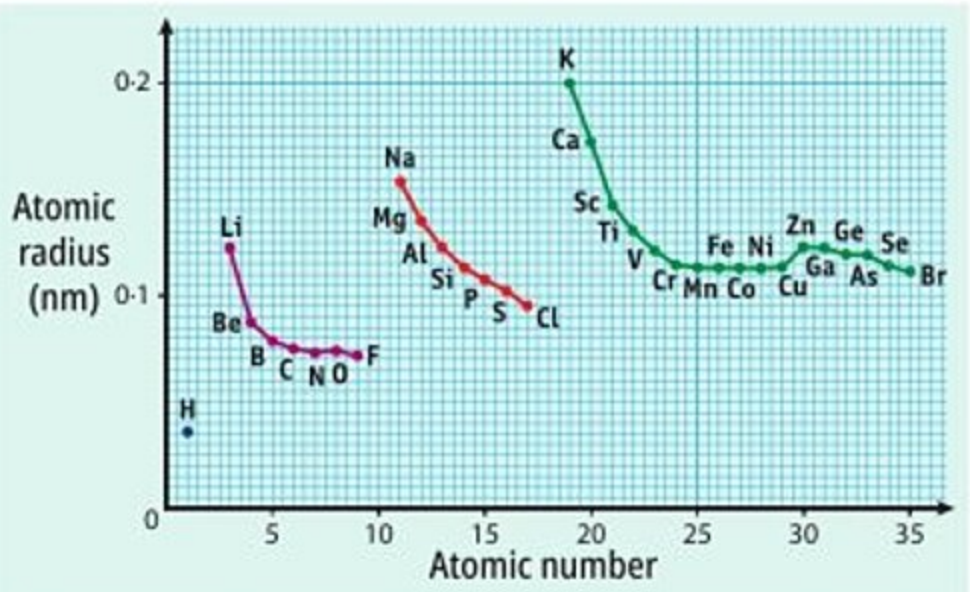


Figure 7.3 The values of atomic radii decrease along any one period, e.g. from lithium to fluorine and from sodium to chlorine. Note also that the values of atomic radii increase down any one group, e.g. from lithium to sodium to potassium.

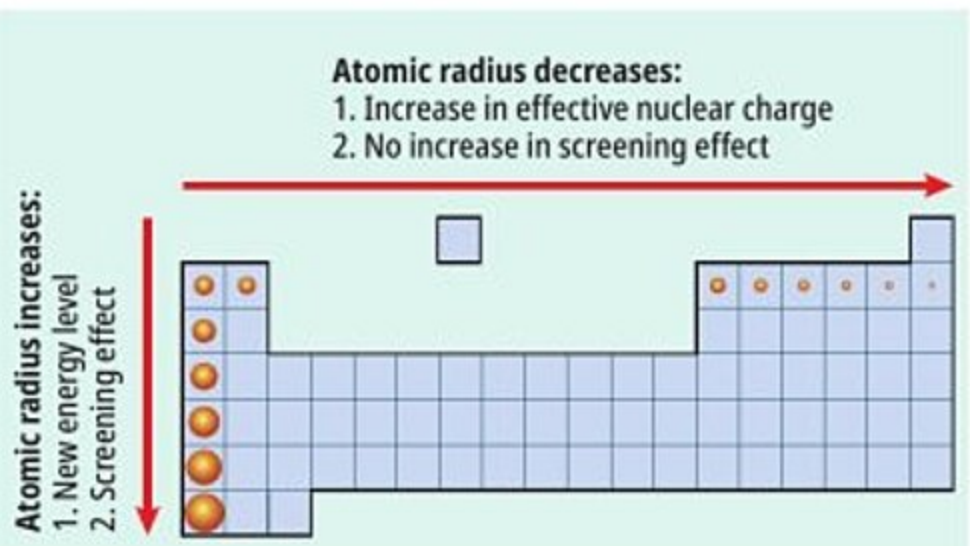

Atomic radius decreases:
1. Increase in effective nuclear charge
2. No increase in screening effect
Atomic radius increases:
1. New energy level
2. Screening effect

Figure 7.4 Atomic radius values decrease along the periods and increase down the groups.

The values of the **atomic radius increase down the groups** in the Periodic Table for two reasons:

1. **New energy level**

- As you move down a group in the Periodic Table, the additional electrons are going into a **new energy level** (orbit) which is further from the nucleus, e.g. in lithium the electrons are being added to the $n = 2$ energy level, and in sodium they are being added to the $n = 3$ energy level.
- With each extra energy level (orbit) the outer electrons are becoming further away from the nucleus, i.e. the atomic radius increases.

2. **Screening effect of inner electrons**

- You might expect that since the nuclear charge increases down a group, there would be an increased attractive force on the outer electrons, causing the atomic radius to get smaller.
- However, even though the nuclear charge increases going from, say, lithium to sodium to potassium, the influence of the increase in the nuclear charge is lessened because of what is called a **screening effect**.
- In an atom with one electron, that electron experiences the full attractive force of the positive nucleus.
- However, in an atom with many electrons, the electrons in the inner energy level or levels help to screen or shield the outer electrons from the positive charge in the nucleus, Figure 7.5.
- Thus, some of the attractive force of the positive charges in the nucleus is lessened by the inner energy levels of electrons.
- Therefore, even though the nuclear charge increases, the increase is counteracted by the increase in the shielding effect of the inner energy levels of electrons.
- Therefore, the atomic radius increases for the reason given in point 1 (above).

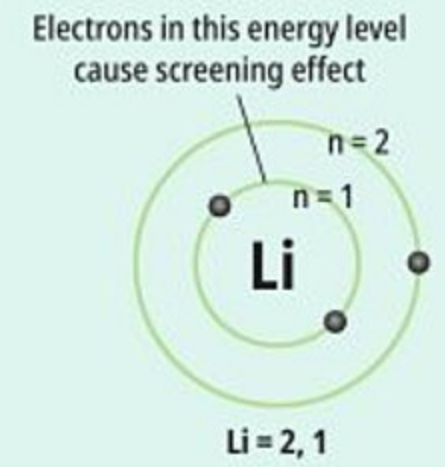


Figure 7.5 The increase in the nuclear charge is counteracted by the increase in the screening effect of the inner electrons.

The values of the **atomic radius decrease across a period** in the Periodic Table for two reasons:

1. **Increase in effective nuclear charge**
   - The number of protons in the nucleus increases from left to right across any one period in the Periodic Table.
   - This means that there is a greater attractive force on the outer electrons.
   - The increased nuclear charge tends to draw the energy levels closer to the nucleus.
   - As this attractive force increases from left to right across the Periodic Table, the nucleus pulls the outer electrons closer to it.
   - Therefore, the atoms become smaller, i.e. the atomic radius decreases.
2. **No increase in the screening effect**
   - In moving from left to right across any one period in the Periodic Table, the extra electrons being added are going into the **same** outer energy level as the previous electron.
   - Therefore, there is no increase in the screening effect caused by the electrons in the inner energy levels. (For the $n = 1$ energy level, there is no screening effect at all by inner electrons. Beyond the $n = 1$ energy level, there is a screening effect but there is no increase in it along any one period.) For example, as we move across period 2, all electrons are being added to the same $n = 2$ energy level (orbit or shell). Since electrons are being added to the same energy level, there is **no increase in the number of inner energy levels** to cause additional shielding.
   - As there is no additional energy level of electrons being added to counteract the increasing attractive force of the nucleus, the size of the atom shrinks, i.e. the atomic radius decreases.

In short, the atomic radius decreases across a period since there is an increasing number of protons but no increase in the screening effect. Therefore, there is an increase in the effective nuclear charge. This increase in the effective nuclear charge pulls the outer electrons closer to the nucleus and reduces the overall size of the atom.

Note that in the above explanation, we have used the phrase ***increase in effective nuclear charge***. This phrase refers to the net positive charge pulling the electrons towards the nucleus. The effective nuclear charge is obtained by subtracting the effect of the screening electrons from the effect of the positive charge of the nucleus. When the number of protons in the nucleus is increasing without any increase in the screening effect of the electrons in the inner energy levels, we say that there is an **increase in the effective nuclear charge**. Remember this phrase!

TEST YOURSELF: Attempt Questions 7.1–7.2 and W7.1.

7.3 Trends in ionisation energy

We now need to study a topic that helps us to understand why some elements are highly reactive and others are very unreactive. For example, sodium and potassium are very reactive and have to be stored under oil to prevent them from reacting with the air. The reason that they are so reactive is because they lose their outer electrons very easily. On the other hand, silver and gold have very little tendency to lose their outer electrons and hence are very unreactive.

In order to measure the tendency of an atom to lose an electron, chemists define a term called the *first ionisation energy*.

The **first ionisation energy** of an atom is the minimum energy required to completely remove the most loosely bound electron from a neutral gaseous atom in its ground state.

We could represent the first ionisation energy of sodium by the equation:

$$Na^{+}_{(g)} \rightarrow Na^{2+}_{(g)} + e^{-}$$

For example, the first ionisation energy of sodium is 496 kJ mol^{-1}. The symbol mol^{-1} reads 'per mole' and can also be written as kJ/mol. This means that it takes 496 kilojoules of energy to remove the most loosely bound electron from a certain number of atoms of sodium. We will explain the meaning of the chemistry term *mole* in the next chapter. In chemistry, it refers to a certain number of atoms – it has nothing to do with the furry animal!

The symbol *(g)* indicates the gaseous state.

A table of first ionisation energy values is given in Figure 7.6. Note that the term ***first*** *ionisation energy* is only being discussed here. We shall discuss other categories of ionisation energy later in this chapter.

Ionisation energy increases:
1. Increasing effective nuclear charge
2. Decreasing atomic radius

Ionisation energy decreases:
1. Increasing atomic radius
2. Screening effect

H 1312																	He 2372
Li 520	Be 900											B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081
Na 496	Mg 738											Al 578	Si 789	P 1012	S 1000	Cl 1251	Ar 1521
K 419	Ca 590	Sc 631	Ti 658	V 650	Cr 653	Mn 717	Fe 759	Co 758	Ni 737	Cu 746	Zn 906	Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351
Rb 403	Sr 550	Y 616	Zr 660	Nb 665	Mo 685	Tc 702	Ru 711	Rh 720	Pd 805	Ag 731	Cd 868	In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170
Cs 376	Ba 503	La 538	Hf 680	Ta 761	W 770	Re 760	Os 840	Ir 880	Pt 870	Au 890	Hg 1007	Tl 589	Pb 716	Bi 703	Po 812	At 890 ±40	Rn 1037
Fr 380	Ra 509	Ac 499															

Figure 7.6 The first ionisation energies of the elements (in kJ mol^{-1}). Note that ionisation energy values decrease down the groups and increase along the periods.

Ionisation energy values are obtained from the emission spectra of atoms. If you examine the values of the ionisation energies in Figure 7.6, a definite pattern emerges. In general, ionisation energy values decrease down the groups and increase along the periods in the Periodic Table. In an exam, if you cannot remember this trend, simply look up the table of ionisation energies in the *Formulae and Tables* booklet of the State Examinations Commission.

The values of **the first ionisation energy decrease down a group** in the Periodic Table for two reasons:

1. **Increasing atomic radius**
   - As already discussed, the atomic radius increases as you move down any one group.
   - This means that the outermost electrons are becoming further away from the attractive force of the nucleus.
   - Therefore, it becomes easier to remove an electron from the outer energy level.
   - Therefore, the ionisation energy values decrease.
2. **Screening effect of inner electrons**
   - Although the nuclear charge increases down a group, this increase in nuclear charge is essentially cancelled out by the corresponding increase in the screening effect of the intervening energy levels (shells) of electrons.
   - Therefore, the outermost electrons are somewhat shielded from the attractive force of the positively charged nucleus.
   - Therefore, the outermost electrons are easier to remove.
   - Therefore, the ionisation energy values decrease.

The values of **the first ionisation energy increase across a period** in the Periodic Table for two reasons:

1. **Increasing effective nuclear charge**
   - Moving from left to right across the Periodic Table, the number of protons in the nucleus increases.
   - Therefore, the attraction between the nucleus and the outer electrons is steadily increasing without any corresponding increase in screening by electrons in inner energy levels.
   - Therefore, the electrons are being held more firmly.
   - Therefore, it requires more energy to remove one of the electrons from the outermost energy level.
   - Therefore, the ionisation energy values increase.
2. **Decreasing atomic radius**
   - As already discussed, within any period in the Periodic Table, the atomic radius decreases from left to right.
   - Therefore, an electron in the outermost level is becoming closer to the nucleus.
   - Therefore, it is more difficult to remove the electron due to the increased attraction between it and the nucleus.
   - Therefore, the ionisation energy values increase.

Studying Figure 7.7 will help you to understand this.

If you look at Figure 7.7 you will notice that the alkali metals are the elements with the lowest first ionisation energies. Therefore, these metals tend to lose electrons readily and this makes them very reactive. On the contrary, the elements with the highest first ionisation energy values are the noble gases. Since these gases have very little tendency to lose electrons, they are very unreactive.

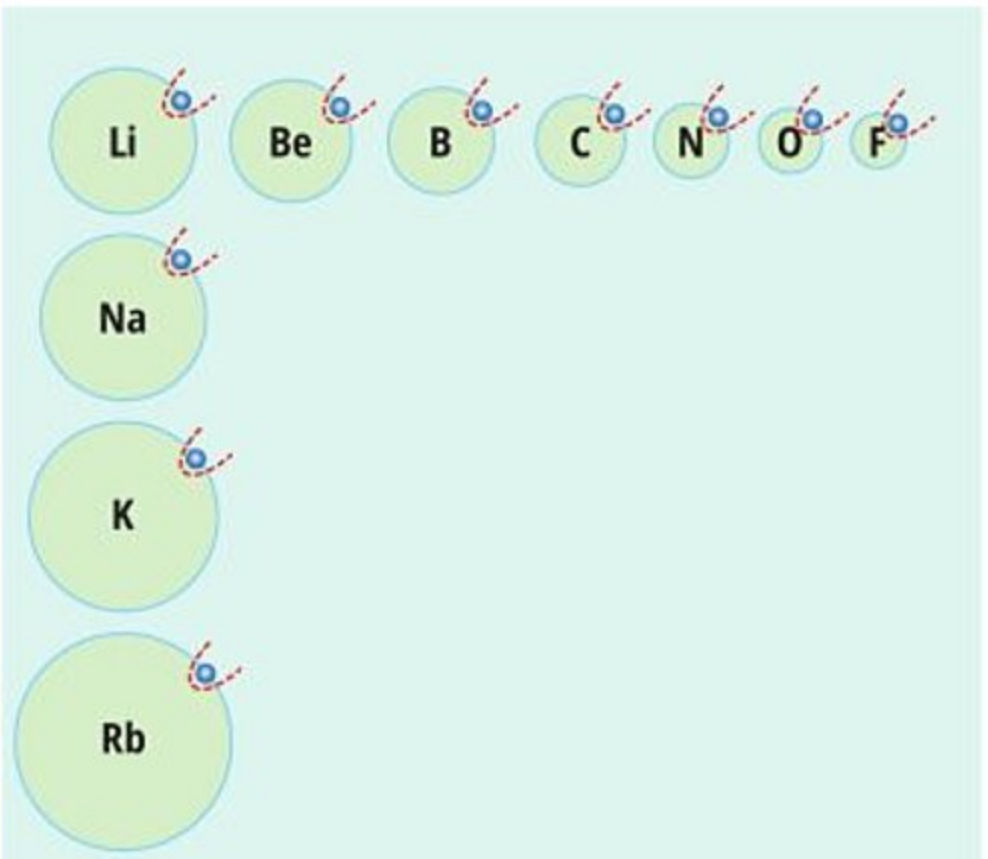


Figure 7.7 The increasing atomic radius down the groups makes it easier to remove an outer electron. The decreasing atomic radius along the periods makes it more difficult to remove an outer electron. The dotted line indicates that an electron is being removed from the outer energy level.

Exceptions to the general trend across a period

If a graph of first ionisation energy versus atomic number is plotted for the first 37 elements, Figure 7.8, it is clear that within any one period some elements do not follow the trend of a smooth increase.

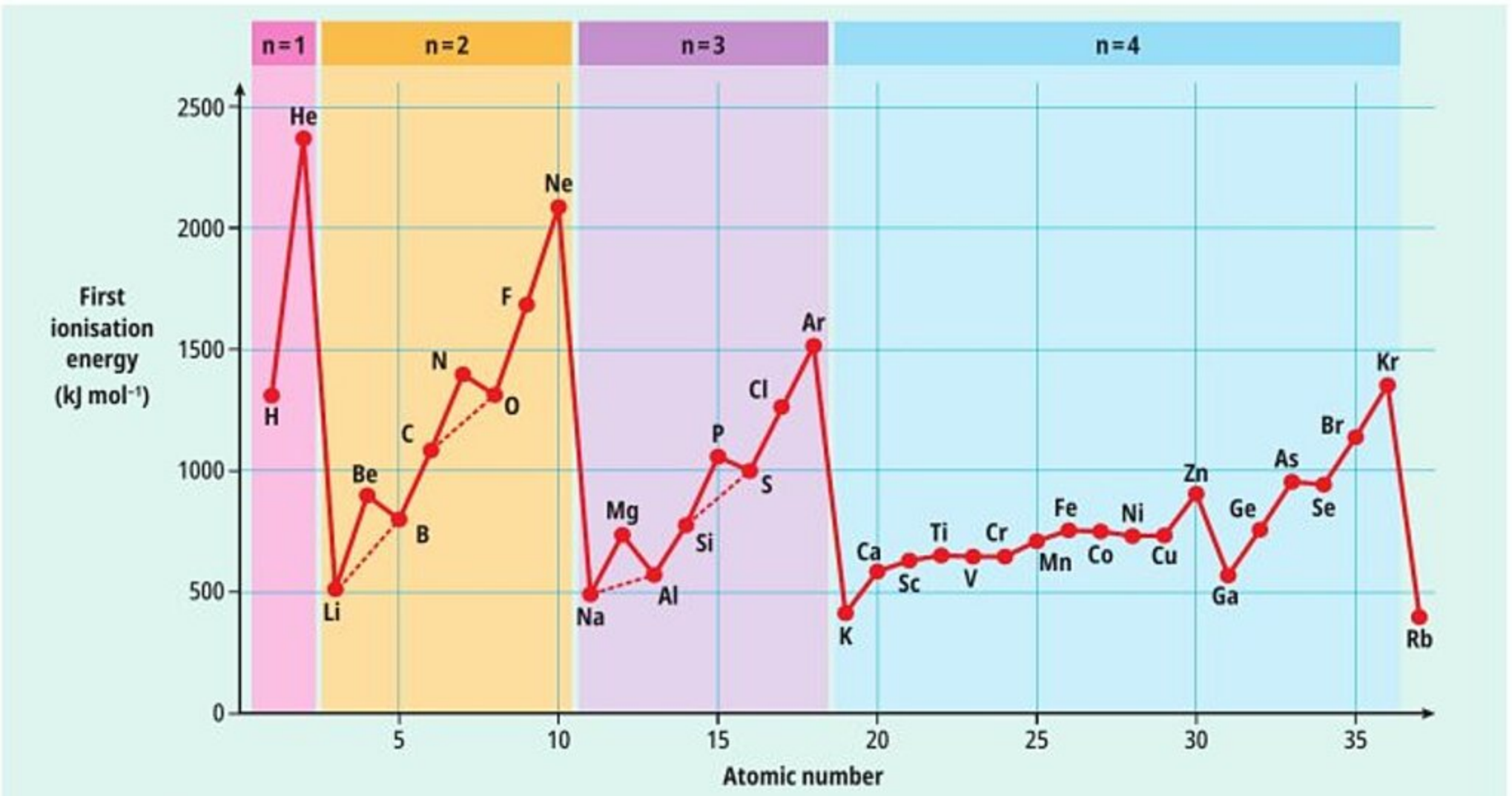


Figure 7.8 Plot of first ionisation energy versus atomic number. Note that in the $n = 2$ period, beryllium and nitrogen have higher values than expected. Also in the $n = 3$ period, magnesium and phosphorus have higher values than expected.

- In the $n = 2$ period, beryllium and nitrogen have higher values than expected.
- The value for beryllium might be expected to lie on the dotted line between that of lithium and boron.
- Similarly, the value for nitrogen might be expected to lie on the dotted line between that of carbon and oxygen.
- It is clear from Figure 7.8 and from the values given in Figure 7.6 that the values for the first ionisation energies of beryllium and nitrogen are much higher than expected.
- Note also that in the $n = 3$ period, the values for the first ionisation energies of magnesium and phosphorus are much higher than expected.
- These irregularities in first ionisation energy trends are explained by the fact that **any sublevel that is completely filled** (as is the case with beryllium and magnesium) **or exactly half filled** (as is the case with nitrogen and phosphorus) **has extra stability**.

Completely filled sublevel

Be = $1s^2, 2s^2$

Mg = $1s^2, 2s^2, 2p^6, 3s^2$

In beryllium, the 2s sublevel is completely filled. In magnesium, the 3s sublevel is completely filled.

- Completely filled s sublevels give a stable electron configuration.
- Therefore, removing an electron from a stable s sublevel requires more energy.
- Therefore, the ionisation energy is higher.

Half-filled sublevel

N = $1s^2, 2s^2, 2p^3$

P = $1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

- In nitrogen, the 2p sublevel is exactly half filled. In phosphorus, the 3p sublevel is exactly half filled.
- Half-filled sublevels have extra stability.
- Therefore, removing an electron from a sublevel that is exactly half filled requires more energy.
- Therefore, the ionisation energy is higher.

Further evidence for the existence of energy levels: successive ionisation energies

So far we have only discussed first ionisation energy. The term ***first*** *ionisation* is so called because it involves the removal of only one electron. However, it is also possible to have second, third, fourth, etc. ionisation energies. The ***second*** *ionisation* energy of an element refers to the removal of a second electron from the positive ion formed after the first electron has been removed. For example, the second ionisation energy of sodium may be represented by the equation:

$$Na^{+}_{(g)} \rightarrow Na^{2+}_{(g)} + e^{-}$$

In Chapter 3, we discussed the spectroscopic evidence for the existence of energy levels. We will now look at additional evidence for the existence of energy levels.

- Evidence for the fact that electrons are arranged in energy levels of different energies is also provided by studying the values of a number of ionisation energies of any one particular element.
- Suppose we measure the first, second and third – up to the nineteenth – ionisation energy of potassium, Figure 7.9.
- Note that the ionisation energy values become so large that it is necessary to take the log of the values to condense the graph into a smaller space.
- To help explain the meaning of this graph, we have labelled the parts of the graph with the letters A–G.
- It will help us to understand the graph if we keep the electron configuration of potassium in mind.

$K = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^1$

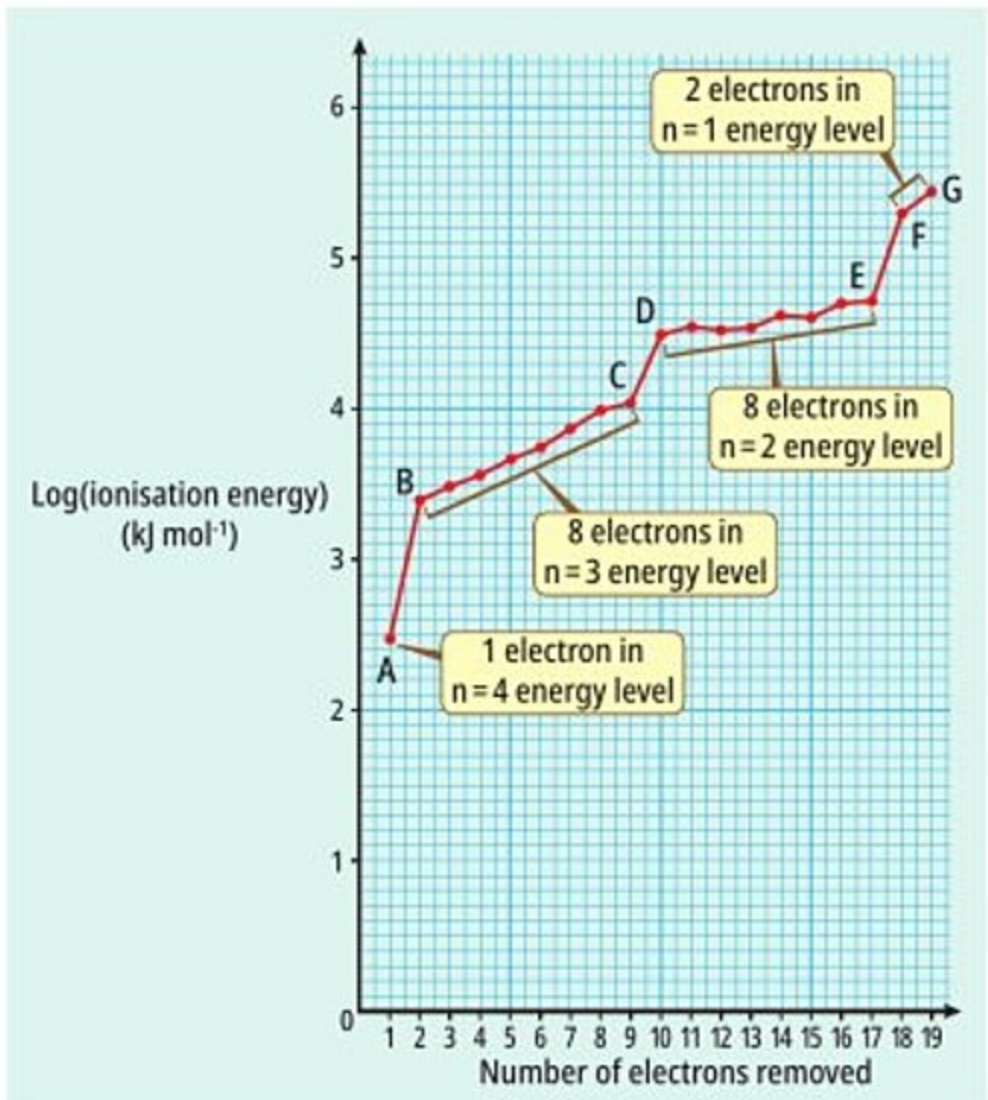


Figure 7.9 Plot of log of ionisation energy versus number of electrons removed from an atom of potassium. This graph provides very good evidence for the existence of energy levels.

Two things are apparent from the graph. Firstly, with each electron removed, the ionisation energy increases. Secondly, the graph is not smooth, as there are peaks in it. The evidence for the existence of energy levels may be summarised as follows:

At A, the one electron in the $n = 4$ energy level has been removed from potassium. The energy required to do this is the first ionisation energy. This has the lowest ionisation energy value, since the electron in the 4s sublevel is easiest to remove.

Moving from A to B on the graph, note the following:

- The second electron is much more difficult to **remove for two reasons:**

1. **The electron is being removed from the $n = 3$ energy level of the K^+ ion, which is closer to the nucleus :**

$K^+ = 1s^2, 2s^2, 2p^6, 3s^2, 3p^6$

Since the second electron is closer to the nucleus ($n = 2$ energy level) than the electron removed from the K atom ($n = 4$), this takes more energy.

2. Note that the electron configuration of K^+ is the same as that of argon. Argon has stable, noble gas configuration. The filled outer energy sublevel ($3p^6$) has extra stability and therefore will require significantly more energy to remove electrons from it.

- The huge increase in the value of the second ionisation energy compared with the first ionisation energy suggests that the second electron being removed must be significantly closer to the nucleus and experiences less shielding.
- Therefore, we have very good evidence for the existence of a lower energy level ($n = 3$ energy level) as the second ionisation energy value, point B on the graph, is considerably higher than the first ionisation energy. These values and the corresponding chemical equations are shown in Table 7.1.

	Value (kJ mol^{-1})	Equation
First ionisation energy	418	$K_{(g)} \rightarrow K^+_{(g)} + e^-$
Second ionisation energy	3050	$K^+_{(g)} \rightarrow K^{2+}_{(g)} + e^-$

Table 7.1 First and second ionisation energy values of the element potassium

We can now give a definition of second ionisation energy.

Second ionisation energy is the energy required to remove an electron from an ion with one positive charge in the gaseous state, i.e. the energy required to carry out the following: $X^+_{(g)} \rightarrow X^{2+}_{(g)} + e^-$.

Note: It is very important that you include the state symbol (g) in writing the above equations, since the definition of ionisation energy refers to the gaseous state.

For your convenience, Figure 7.9 is reproduced on this page.

Moving from B to C on the graph, note the following:

- From B to C, we are removing eight more electrons from the $n = 3$ energy level.
- The removal of the third electron may be represented as follows:

Third ionisation energy (4560 kJ mol^{-1}):

$$K^{2+}_{(g)} \rightarrow K^{3+}_{(g)} + e^-$$

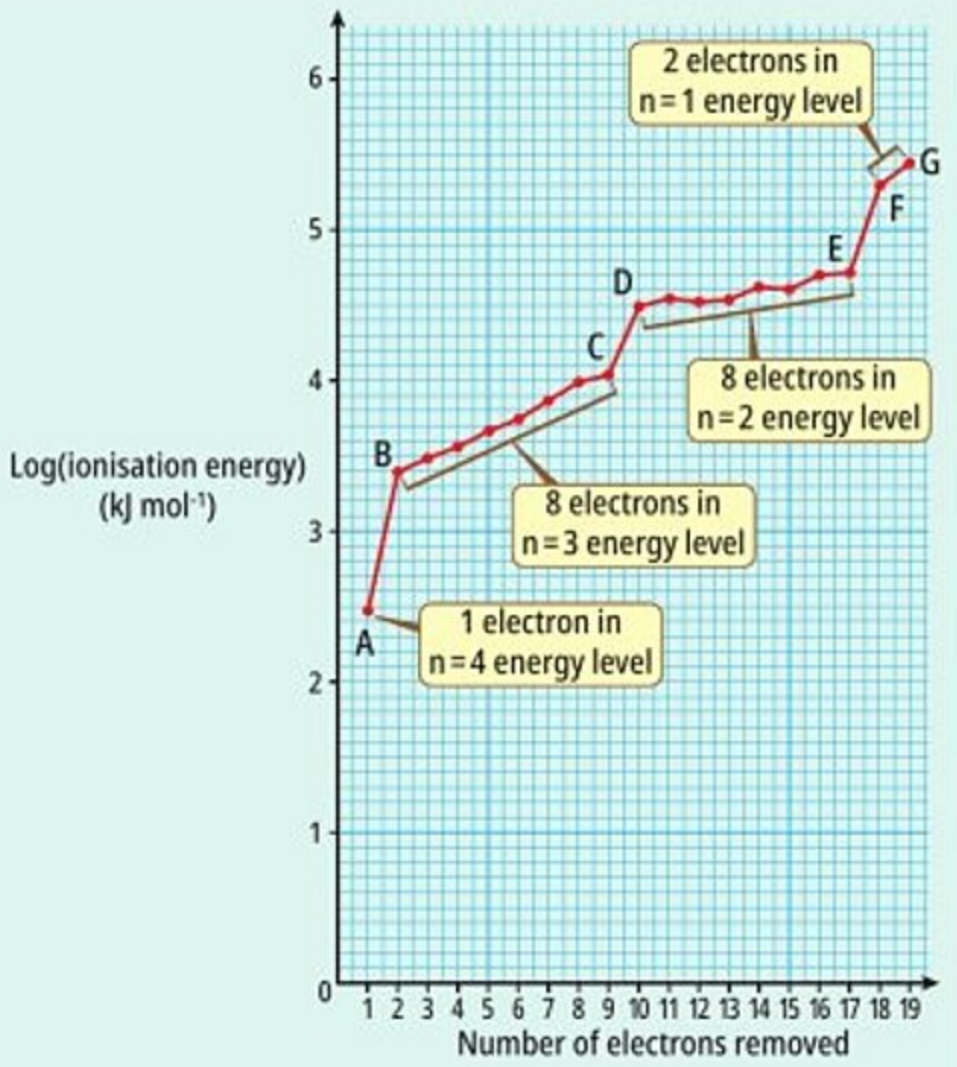


Figure 7.9 Plot of log of ionisation energy versus number of electrons removed from an atom of potassium. This graph provides very good evidence for the existence of energy levels.

- The values steadily increase as we remove the eight electrons from the $n = 3$ energy level.
- After removing the eight electrons in the $n = 3$ energy level, (point C on the graph) there is another very large jump in the value of the ionisation energy for the next electron.
- This implies that the electron at D is being removed from an energy level that is closer to the nucleus i.e. the $n = 2$ energy level. (This increase is actually much larger than it appears from the graph. Due to the logarithmic scale, the jump is actually greater by a factor of ten.)
- Since an electron is being removed from the filled $2p^6$ sublevel, a lot of energy is needed as this full sublevel has extra stability.
- This ion (C on graph) has the same electron configuration as neon.

$$K^{9+} = 1s^2, 2s^2, 2p^6$$

Moving from D to E on the graph, note the following:

- From D to E, we are removing the eight electrons in the $n = 2$ energy level.
- At E there is again a very large jump, as we remove electrons from an energy level that is closer to the nucleus, i.e. the $n = 1$ energy level.
- The ion at E has the same electron configuration as helium. Since the $1s^2$ sublevel is filled, it has extra stability and more energy is needed to remove the electron.
- At G we have removed all 19 electrons.

Two general points emerge from this study:

1. There is a steady increase in ionisation energy values as electrons are removed from an atom. There are two reasons for this steady increase:
   - **(a)** For each electron that is removed, the size of the positive charge on the ion that is left behind increases by one. Therefore, there is a greater attraction between the positive nucleus and the remaining electrons.
   - **(b)** It is found that a positive ion is smaller than the neutral atom from which it has been formed. Therefore, the electrons remaining behind in the positive ion are closer to the nucleus and thus more strongly attracted to the nucleus. With the removal of each successive electron, the size of the positive charge on the ion increases and the next electron to be removed will be closer to the nucleus.
2. There is a large increase in ionisation energy whenever an electron is removed from a new energy level and a reasonably substantial increase in the case of an electron being removed from a new sublevel. This is because filled sublevels have extra stability, i.e. it requires more energy to remove electrons from a filled sublevel.

Example 7.1

Question

The first four ionisation energies of the element of atomic number 5 are shown in Table 7.2.

(a) Explain why the second ionisation energy is greater than the first.

(b) Explain why the increase in ionisation energy is relatively small for the third electron but very large for the fourth electron. [LCH]

Electron removed	Ionisation energy (kJ mol^{-1})
1st	799
2nd	2421
3rd	3650
4th	24962

Table 7.2

Answer

(a) An atomic number of 5 (boron) indicates that the atom has five electrons.

- The second ionisation energy is always greater than the first because the second electron is being removed from a positively charged ion.
- The electrons are held more firmly in a positively charged ion than in the corresponding neutral atom, because a positive ion is smaller than the neutral atom from which it is formed.
- Since the electrons are closer to the nucleus, more energy is required to remove them.
- Therefore, the second ionisation energy is greater than the first ionisation energy.

(b)

- The third electron, like the second electron, is being removed from the $n = 2$ energy level.
- Therefore, the increase in ionisation energy is fairly small.
- However, the fourth electron is being removed from the $n = 1$ energy level.
- Since the $n = 1$ energy level is nearer the nucleus than the $n = 2$ energy level, it requires a lot more energy to remove the electron from the $n = 1$ energy level.
- Also, the fourth electron is being removed from the filled $n = 1$ energy level ($1s^2$ electron configuration) which is very stable. This ion has the same electron configuration as helium

  $B^{3+} = 1s^2$
- Therefore, extra energy will have to be supplied to remove this electron.
- Therefore, the increase in ionisation energy is very large for the fourth electron.

» Study Example 7.2 in the online resources.

TEST YOURSELF: Attempt Questions 7.3–7.5 and W7.2–W7.6.

7.4 Trends in electronegativity

In Chapter 6, we discussed electronegativity and learned that electronegativity is **the relative attraction that an atom in a molecule has for the shared pair of electrons in a covalent bond**. From studying the table of electronegativity values (Figure 6.3, p.77) we saw that elements such as fluorine and chlorine on the right-hand side of the Periodic Table have high electronegativity values. On the other hand, elements such as potassium and sodium on the left-hand side of the Periodic Table have low electronegativity values.

We now examine the trends in electronegativity values in the Periodic Table and explain the reasons for these trends. In general, electronegativity values decrease down the groups and increase along the periods, Figure 7.10.

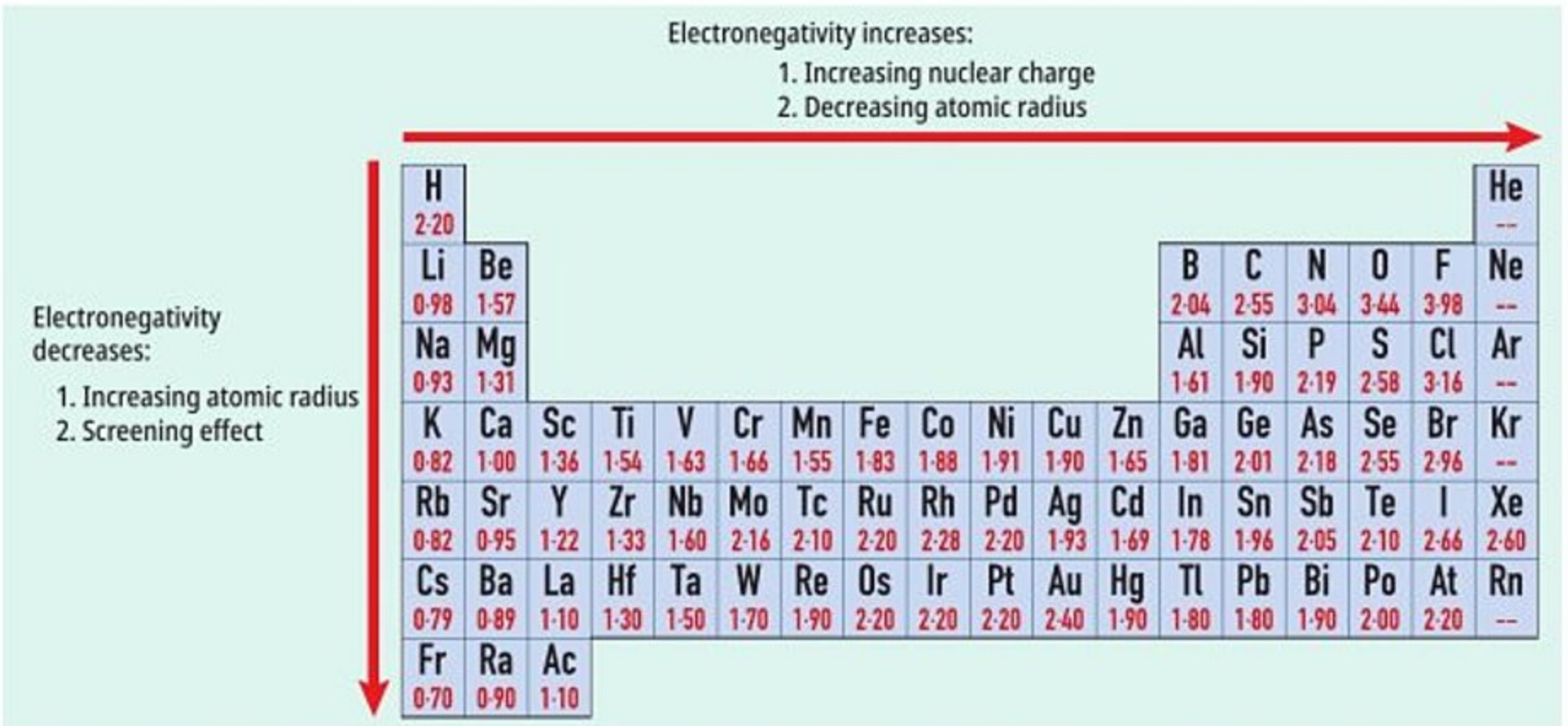


Figure 7.10 Electronegativity values decrease down the groups and increase along the periods.

The values of **electronegativity decrease down the groups** in the Periodic Table for two reasons:

1. **Increasing atomic radius.**
   - As already discussed, the atomic radius increases as you move down any one group.
   - Therefore, the outermost electrons are becoming further and further away from the attractive force of the nucleus.
   - Therefore, there is a smaller attraction between the nucleus and the shared pair of electrons.
   - Therefore, the electronegativity decreases.
2. **Screening effect of inner electrons.**
   - Although the nuclear charge increases down a group, this increase in nuclear charge is essentially cancelled out by the increase in screening effect of the added intervening energy levels of electrons.
   - Therefore, the outermost electrons are somewhat shielded from the attractive force of the positively charged nucleus.
   - Since it is these outermost electrons that are involved in bonding, the attraction of the nucleus for these electrons decreases going down the group.
   - Therefore, the electronegativity decreases.

The values of **electronegativity increase across the periods** in the Periodic Table for two reasons:

1. **Increasing effective nuclear charge.**
   - Moving from left to right across the Periodic Table, the number of protons in the nucleus (nuclear charge) increases. Also, there is no increase in the screening effect.
   - Therefore, the attraction between the nucleus and the outer electrons is steadily increasing.
   - Therefore, the electrons involved in bonding are being more strongly attracted to the nucleus.
   - Therefore, the electronegativity increases.
2. **Decreasing atomic radius.**
   - As already discussed, within any period in the Periodic Table, the atomic radius decreases from left to right.
   - Therefore, the electrons in the outermost level are becoming closer to the nucleus.
   - Therefore, there is a greater attraction between the nucleus and these outer electrons.
   - Therefore, the electronegativity increases.

NOTE

Note that the trends in electronegativity generally follow the same pattern as those of ionisation energy. Electronegativity values are not assigned to the noble gases, as these elements have no tendency to form bonds and so the definition of electronegativity does not apply to them. The trends in electronegativity may easily be deduced from the tables shown in the *Formulae* and *Tables* booklet available to you in state exams.

So far we have seen that there is a definite repeating pattern or periodicity associated with atomic radii, ionisation energies and electronegativities of the elements. We now consider how the chemical properties of certain groups of elements are affected by these trends.

The trends in electronegativity are clearly seen in a graph of electronegativity versus atomic number, Figure 7.11.

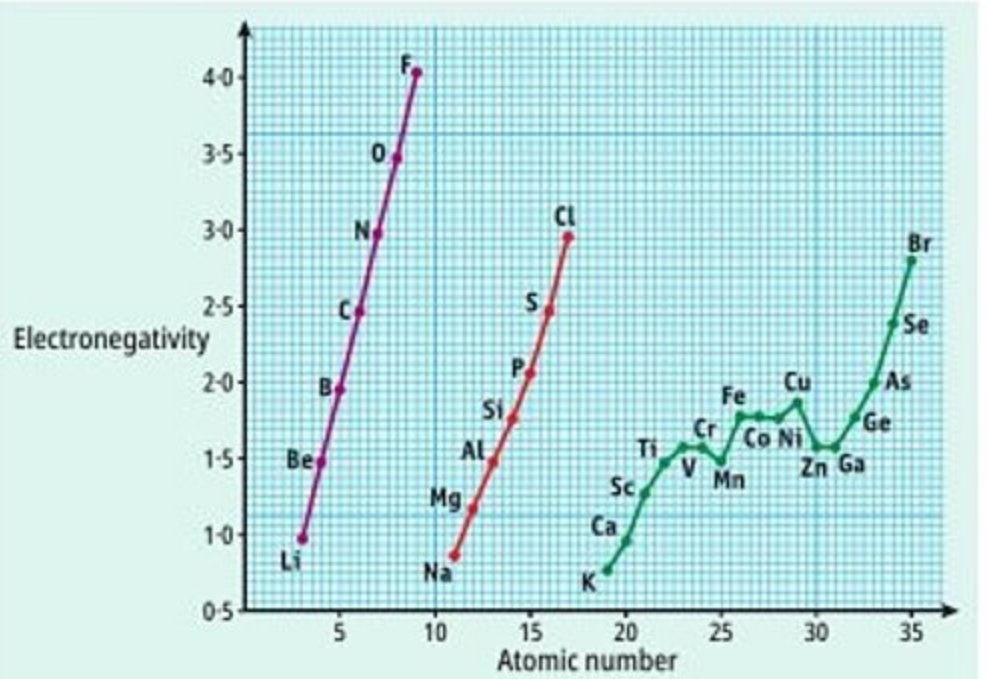


Figure 7.11 Plot of electronegativity values versus atomic number for the first 35 elements. Note the increase along any one period, e.g. lithium to fluorine, sodium to chlorine, or potassium to bromine. Note also the decrease down the groups, e.g. fluorine to chlorine to bromine, and lithium to sodium to potassium.

7.5 Properties of four groups in the Periodic Table

In our study of chemical bonding in Chapter 5, we have seen how bonds are formed when chemical reactions occur. In the case of ionic bond formation, the bonds are formed by the transfer of an electron (or electrons) from the outermost energy level of one atom to that of another atom. In the case of covalent bond formation, the bonds are formed by the sharing of electrons between outermost energy levels of adjacent atoms.

The chemical properties of elements are largely determined by the number of electrons in the outermost energy level. For example, all of the elements in Group 1 (the alkali metals) have one electron in their outermost energy level. As a result of this, all of these elements have similar chemical properties. Similarly, all of the elements in Group 17 (or VII) have seven electrons in their outermost energy level. As a result of this, all of these elements also have similar chemical properties.

To illustrate this similarity of elements in the same group (family), we now consider some of the properties of four groups (families) of elements: the alkali metals (Group 1), the alkaline earth metals (Group 2), the halogens (Group 17) and the noble gases (Group 18). These are the four groups that are specified in the Leaving Certificate chemistry curriculum – so study these groups carefully!

7.5.1 Group 1: The alkali metals

The alkali metals are located in Group 1 of the Periodic Table. They are called 'alkali' metals because they form alkaline or basic solutions when added to water. The three alkali metals on your course are lithium, sodium and potassium, Figure 7.12. As they are all very reactive, they have to be stored under oil to prevent them coming in contact with oxygen in the air and with water. The main properties of the alkali metals are summarised in Table 7.4

Figure 7.12 (a) Lithium metal. Note that lithium has a very low density and floats on oil. (b) Sodium metal is a soft metal and can be cut with a knife. After cutting, the shiny metal is quickly covered with a white coating of sodium oxide. (c) Potassium metal is shiny when cut, but very quickly reacts with oxygen in the air to form potassium oxide.

The properties of the alkali metals may be summarised as follows:

- All of the alkali metals are **very reactive** elements because they all have low first ionisation energy values, i.e. they readily lose the single electron in the outer energy level.
- They are so reactive that none of them occurs free in nature as the uncombined metal itself. The alkali metals in your school laboratory have been extracted from their compounds.
- Since the alkali metals have low first ionisation energies and low electronegativity values, they readily form ionic compounds by losing their single outer electron.
- By losing the single outer electron, potassium obtains the stable arrangement of eight electrons in its outer energy level. In other words, the octet rule is satisfied since potassium now has the electron configuration of the noble (inert) gas argon.
- The tendency to lose an electron is observed in all of the chemical reactions of the alkali metals.
- The reaction of the alkali metals with water illustrates very nicely the trend of increasing reactivity down the group. As shown in Table 7.4, all of the alkali metals react with water
- Lithium reacts quite vigorously with water, sodium more vigorously and potassium even more vigorously. In fact, the reaction is so vigorous in the case of potassium that the heat generated by the reaction causes the hydrogen gas given off in the reaction to catch fire.
- This increase in reactivity reflects the decrease in ionisation energy values down the group.

Rubidium and caesium react so violently with water that their reactions are too dangerous to demonstrate. Professor Martyn Poliakoff, has made videos about every element in the Periodic Table and these are worth viewing online. Even though you will not have rubidium and caesium in your school laboratory, you can watch the very violent reactions online.

Note: The reaction of the alkali metals with dilute acids is so dangerous that it must never be attempted. So much hydrogen is released in such a short time that an explosion occurs.

Group 1: Alkali Metals

Element	State	Conductivity of electricity and heat	Reactivity	Trend in Reactivity
Lithium	Solid	Good	**Reaction with Oxygen** $4Li + O_2 \rightarrow 2Li_2O$ lithium + oxygen → lithium oxide **Reaction with Water** $2Li + 2H_2O \rightarrow 2LiOH + H_2\uparrow$ lithium + water → lithium hydroxide + hydrogen gas	Increasing reactivity ↓
Sodium	Solid	Good	**Reaction with Oxygen** $4Na + O_2 \rightarrow 2Na_2O$ sodium + oxygen → sodium oxide **Reaction with Water** $2Na + 2H_2O \rightarrow 2NaOH + H_2\uparrow$ sodium + water → sodium hydroxide + hydrogen gas	
Potassium	Solid	Good	**Reaction with Oxygen** $4K + O_2 \rightarrow 2K_2O$ potassium + oxygen → potassium oxide **Reaction with Water** $2K + 2H_2O \rightarrow 2KOH + H_2\uparrow$ potassium + water → potassium hydroxide + hydrogen gas	

Table 7.4 Summary of properties of Group 1 elements (Alkali Metals).

7.5.2 Group 2: The alkaline earth metals

The alkaline earth metals are located in Group 2 of the Periodic Table. They are called 'alkaline' earth metals because they form alkaline or basic solutions when added to water. They are called 'earth' metals because many of their compounds are found in the earth. For example, MgO (magnesium oxide) is found in the earth and is commonly called magnesia – hence the name *Milk of Magnesia* used in indigestion remedies. Calcium oxide, CaO, is also found in the earth and is commonly called lime.

The three alkaline earth metals on your course are beryllium, magnesium and calcium, Figure 7.13.

Figure 7.13 The alkaline earth metals (from left) beryllium, magnesium, calcium, strontium and barium.

Beryllium, magnesium and calcium are all shiny, silvery-looking metals. You will not have beryllium in your school laboratory, as it is a very toxic substance.

The main properties of the alkaline earth metals are summarised in Table 7.5.

Group 2: Alkaline Earth Metals

Element	State	Conductivity of electricity and heat	Reactivity	Trend in Reactivity
Beryllium	Solid	Good	**Reaction with Oxygen** $2Be + O_2 \rightarrow 2BeO$ beryllium oxygen beryllium oxide **Reaction with Water** no reaction	Increasing reactivity ↓
Magnesium	Solid	Good	**Reaction with Oxygen** $2Mg + O_2 \rightarrow 2MgO$ magnesium oxygen magnesium oxide **Reaction with Water** $Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2\uparrow$ magnesium water magnesium hydroxide hydrogen gas *Reaction is slow with cold water but much faster with steam*	
Calcium	Solid	Good	**Reaction with Oxygen** $2Ca + O_2 \rightarrow 2CaO$ calcium oxygen calcium oxide **Reaction with Water** $Ca + 2H_2O \rightarrow Ca(OH)_2 + H_2\uparrow$ calcium water calcium hydroxide hydrogen gas *Reacts quickly with cold water*	

Table 7.5 Summary of properties of Group 2 elements (Alkaline Earth Metals).

The properties of the alkaline earth metals may be summarised as follows:

- All the alkaline earth metals are reactive elements because they have low first ionisation energy values, i.e. they readily lose the two electrons in their outermost energy level.
- They are less reactive than the alkali metals but still too reactive to occur freely in nature as pure metals. Instead, they are found in stable compounds such as magnesium oxide and calcium carbonate ($CaCO_3$), which is commonly called limestone.

- Since the alkaline earth metals have low ionisation energies and low electronegativity values, they readily form ionic compounds by losing their two outermost electrons.
- The tendency to lose two electrons is a key feature of all the chemical reactions of the alkaline earth metals, including their reactions with oxygen, water and acids.
- The reaction of alkaline earth metals with water demonstrates the trend of increasing reactivity down the group. Beryllium does not react with water, magnesium reacts slowly with cold water but vigorously with steam, and calcium reacts readily with cold water. This increasing reactivity reflects the decrease in ionisation energy values down the group.

Note: Beryllium is unique among the alkaline earth metals as it forms both ionic and covalent bonds. For example, in BeO the bonding is ionic (E.N. difference = 1.87) and in $BeCl_2$ the bonding is covalent (E.N. difference = 1.59).

Why does the reactivity of the alkali metals and alkaline earth metals increase down the group?

The reactivity of the alkali metals and alkaline earth metals increases down the group because:

- The atomic radius increases.
- The screening effect of inner energy levels of electrons increases.
- The above two factors cause the first ionisation energy to decrease down the group, Figure 7.16.
- Therefore, the electrons in the outermost energy levels are more easily lost.
- Therefore, the reactivity increases down the group.

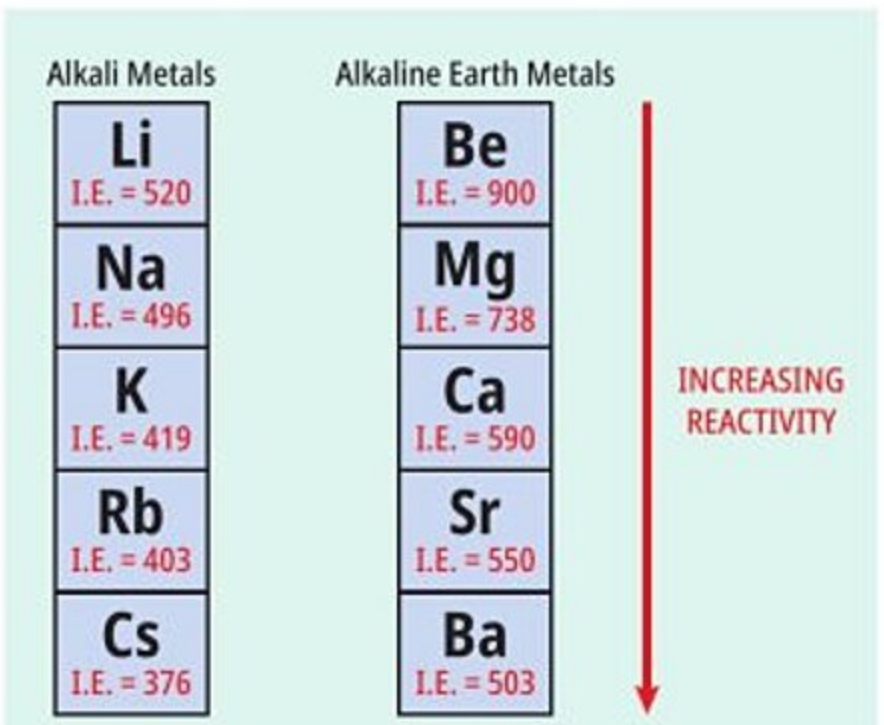


Figure 7.14 The reactivity of the alkali metals and the alkaline earth metals increases down the group because the first ionisation energy decreases down the group. Therefore, the electrons in the outermost energy levels are more easily lost as you move down the group.

7.5.3 Group 17: The halogens

The halogens are located in Group 17 of the Periodic Table, Figure 7.15. The word 'halogen' comes from the Greek language and it means 'producer of salt'. This name is given to the elements of Group 17 because they all react with metals to produce various salts. (We will study salts in more detail in Chapter 11.) You will be familiar with table salt, sodium chloride, NaCl. This compound is formed when the halogen chlorine reacts with the metal sodium.

As discussed in Chapter 6, there are only weak London dispersion forces between the molecules in the halogens. Note in the photograph of bromine that, even though bromine is a liquid at room temperature, bromine vapour fills the flask. This is because bromine has a low boiling point and, therefore, evaporates easily to form a reddish-brown vapour.

The main properties of the halogens are summarised in Table 7.6.

Figure 7.15 Chlorine is a pale green/yellow gas, bromine is a dark-red volatile liquid, and iodine is a purple solid.

Group 17: The Halogens

Element	State	Conductivity of electricity and heat	Reactivity	Trend in Reactivity
Fluorine	Gas	Poor	**Reaction with sodium** $2Na$ (sodium) + F_2 (flourine) → $2NaF$ (sodium flouride) **Reaction with hydrogen** H_2 (hydrogen) + F_2 (flourine) → $2HF$ (hydrogen flouride)	Increasing reactivity
Chlorine	Gas	Poor	**Reaction with sodium** $2Na$ (sodium) + Cl_2 (chlorine) → $2NaCl$ (sodium chloride) **Reaction with hydrogen** H_2 (hydrogen) + Cl_2 (chlorine) → $2HCl$ (hydrogen chloride)	
Bromine	Solid	Poor	**Reaction with sodium** $2Na$ (sodium) + Br_2 (bromine) → $2NaBr$ (sodium bromide) **Reaction with hydrogen** H_2 (hydrogen) + Br_2 (bromine) → $2HBr$ (hydrogen bromide)	
Iodine	Solid	Poor	**Reaction with sodium** $2Na$ (sodium) + I_2 (iodine) → $2NaI$ (sodium iodide) **Reaction with hydrogen** H_2 (hydrogen) + I_2 (iodine) → $2HI$ (hydrogen iodide)	

Table 7.6 Summary of properties of Group 17 elements (the Halogens).

The properties of the halogens may be summarised as follows:

- The halogens contain some highly electronegative elements.
- Since the electronegativity values decrease down the group, this means that fluorine is the most electronegative element of the halogens. In fact, fluorine is the most electronegative element in the Periodic Table.
- Since the halogens have such a great attraction for electrons, they are very reactive.
- The halogens do not exist free in nature, e.g. chlorine gas has to be extracted from one of its compounds such as sodium chloride.
- Fluorine is the most reactive of all the halogens because of its high electronegativity. It is far too reactive to be kept in school laboratories. Most chemists have never seen the element fluorine, as it is so highly reactive.
- Since the halogens are non-metals, they are poor conductors of electricity.

- Note that in Table 7.6, the reaction of each halogen with sodium is the example given, as this is the one most commonly observed, Figure 7.16. However, similar reactions occur with all the other alkali metals and alkaline earth metals.
- An unusual property of iodine is that it does not melt to a liquid when heated. Instead, it changes directly from a solid to a gas. This process is called sublimation. The purple vapour of iodine is easy to see, Figure 7.17.

Sublimation is the changing of a solid directly to a gas on heating without going through the liquid phase.

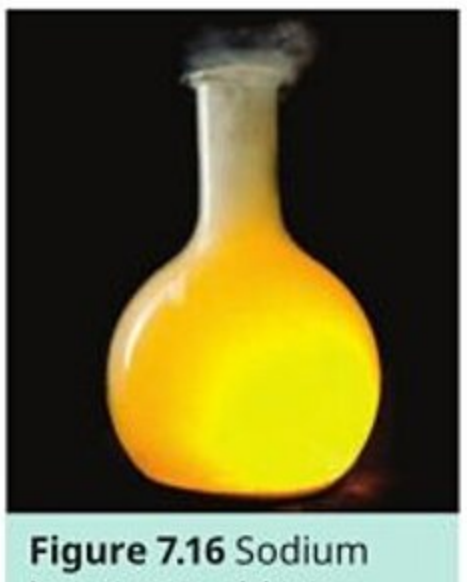


Figure 7.16 Sodium burning in chlorine

Figure 7.17 Some iodine crystals at the bottom of the flask are warmed. Note that purple iodine vapour is formed when the iodine sublimes. Note also that some of the vapour has condensed back to crystals on the cool part of the glass.

Why does the reactivity of the halogens increase up the group?

As shown in Table 7.6, the trend in reactivity of the halogens is in the opposite direction to that of the alkali metals. The reactivity of the halogens increases **up** the group because:

- The atomic radius decreases as you go up the group.
- There is a decrease in the screening effect, as there are fewer inner energy levels as you go up the group.
- The above two factors cause the first ionisation energy to increase up the group.
- Therefore, the electrons in the outermost energy levels are more tightly held as you go up the group. For example, fluorine is the most electronegative element in the Periodic Table. Figure 7.18.
- Therefore, the reactivity increases up the group.

Because of their high electronegativities, the halogens remove electrons easily from other substances. This makes them very reactive. Examples of a halogen taking electrons from a less electronegative halogen may be shown as follows:

- If chlorine gas is bubbled through a solution containing bromide ions, the chlorine takes electrons from the bromide ions, converting them into bromine:

$$\underset{\text{chlorine}}{Cl_2} + \underset{\text{bromide ions}}{2Br^-} \longrightarrow \underset{\text{chloride ions}}{2Cl^-} + \underset{\text{bromine}}{Br_2}$$

colourless **red**

This shows that the electronegativity of the chlorine atom (E.N. = 3.16) is greater than that of the bromine atom (E.N. = 2.96), as the chlorine atom takes an electron from the bromide ion. This reaction is shown happening in one of the videos accompanying this textbook. The colourless solution of bromide ions turns red due to the formation of the red bromine.

If a solution of bromine in water ('bromine water') is added to a solution containing iodide ions, iodine is displaced from the solution. The more electronegative bromine atoms (E.N. = 2.96) take electrons from the less electronegative iodide ions (E.N. = 2.66) as shown in the following equation:

$$\underset{\text{bromine}}{Br_2} + \underset{\text{iodide ion}}{2I^-} \longrightarrow \underset{\text{bromide ion}}{2Br^-} + \underset{\text{iodine}}{I_2}$$

colourless **purple**

Note that in each case **the more reactive halogen displaces the less reactive halogen from the solution of its ions**.

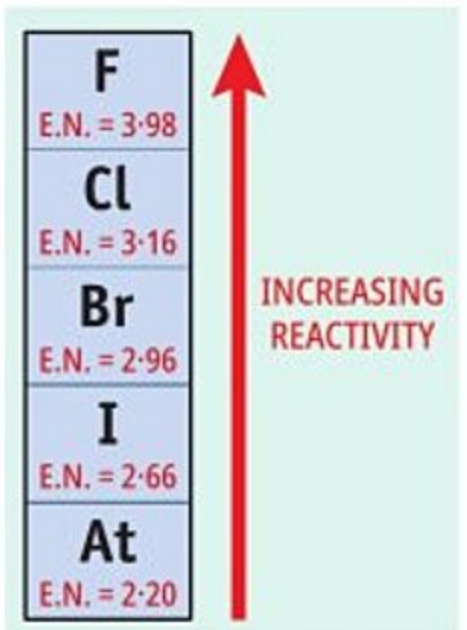


Figure 7.18 The reactivity of the halogens increases up the group. This is because as you move up the group, the electronegativity values increase.

7.5.4 Group 18: The noble (inert) gases

When it comes to studying the chemistry of the noble (inert) gases, you can sit back and relax! The reason for this is that, since they are so unreactive, there is little to study about their chemistry. The noble gases are located in Group 18 of the Periodic Table. With the exception of helium, they all have eight electrons in their outer energy level. Therefore, they are all very stable. Helium has a full outer energy level (He = $1s^2$) and is also very stable.

One of the popular uses of noble gases is in plasma balls, Figure 7.19.

Figure 7.19 Plasma balls usually contain a mixture of the noble gases neon, argon and xenon.

Noble gases are used in plasma balls, as these gases are very unreactive. Therefore, when a high voltage current is passed through the gases, no unwanted side reactions take place. In addition, different colours are given off when electricity is passed through these gases. Helium is probably the best-known noble gas, as it is commonly used to fill balloons.

The properties of the noble gases are summarised in Table 7.7.

Group 18: Noble gases

Element	State	Conductivity of electricity and heat	Reactivity
Helium	Gas	Poor	Unreactive
Neon	Gas	Poor	Unreactive
Argon	Gas	Poor	Unreactive
Krypton	Gas	Poor	Unreactive

Table 7.7 Summary of properties of Group 18 elements (the noble gases)

You may remember in Chapter 6 that we learned that the boiling points of the noble gases increase down the group from helium to radon (Figure 6.19, p.85). We explained that this increase is related to the size of the atoms. The increase in atomic radius means that the electron clouds are getting bigger and so, temporary dipoles are more easily formed, giving rise to stronger London dispersion forces. These stronger forces are more difficult to break. This means that more energy is required to separate the atoms from each other and this causes the increase in boiling points.

TEST YOURSELF: Attempt Questions 7.8 and W7.7–W7.18.

» Study SEC exam question 7.3 and model answer in the online resources.

Summary What I should know

- The atomic radius of an atom is defined as half the distance between the nuclei of two atoms of the same element, which are joined together by a single covalent bond.
- Atomic radius values increase down any one group in the periodic table because the electrons are going into a new energy level that is further from the nucleus and there is an increase in the screening effect by inner electrons.
- Atomic radius values decrease from left to right across a period because of increasing effective nuclear charge and no increase in the screening effect.
- The first ionisation energy of an atom is the minimum energy required to completely remove the most loosely bound electron from a neutral gaseous atom in its ground state.
- Ionisation energy values decrease down the groups because of increasing atomic radius and an increase in the screening effect of inner electrons.
- Ionisation energy values increase along the periods because of increasing effective nuclear charge and decreasing atomic radius.
- Second ionisation energy is the energy required to remove an electron from an ion with one positive charge in the gaseous state, i.e. the energy required to carry out the following:

$$X^{+}_{(g)} \rightarrow X^{2+}_{(g)} + e^{-}$$

- Electronegativity values decrease down a group because of increasing atomic radius and an increase in the screening effect of inner electrons.
- Electronegativity values increase along the periods because of increasing effective nuclear charge and decreasing atomic radius.
- The chemical properties of an element are determined by the number of electrons in the outermost energy level.
- Within the alkali metals, alkaline earth metals and halogen groups of the Periodic Table, there are definite trends in the chemical and physical properties of the elements.

Learning outcomes

At the end of this chapter, I should be able to:

Explain the concept of atomic radius (covalent radius) and discuss the trends in atomic radius in the Periodic Table.	⬡	⬡	⬡
Discuss the trends in ionisation energy in the Periodic Table and account for the exceptions to some general trends.	⬡	⬡	⬡
Explain how successive ionisation energies provide evidence for the existence of energy levels.	⬡	⬡	⬡
Outline the trends in electronegativity in the Periodic Table and explain the reason for these trends.	⬡	⬡	⬡
Interpret the properties of the alkali metals, alkaline earth metals, halogens and noble gases in terms of the above trends.	⬡	⬡	⬡

Chapter review questions

7.1 **(a)** Distinguish between the terms *bond length* and *atomic radius* (*covalent radius*).

(b) Why do tables of atomic radii (covalent radii) not include values for the noble gases?

(c) Explain the phrase 'screening effect of inner electrons'.

(d) How does nuclear charge vary from left to right across the periods in the Periodic Table?

(e) Give reasons why the atomic radius of calcium is smaller than that of potassium.

(f) Explain the term *effective nuclear charge*.

7.2 **(a)** Define atomic radius (covalent radius).

(b) Describe and account for the trend in atomic radii (covalent radii) of the elements:

(i) Across the second period

(ii) Down any group, of the Periodic Table. [LCH]

7.3 **(a)** Write down an equation to represent the first ionisation energy of potassium.

(b) Explain why the first ionisation energy of element 33 is greater ...

(i) Than that of element 32

(ii) Than that of element 34. [LCH]

(c) Beryllium and nitrogen are exceptions to the general increase in ionisation energies shown by the other elements in the period lithium to neon. Explain the reason for this. [LCH]

(d) What names are normally given to the energy changes represented by:

(i) $X \rightarrow X^{+} + e^{-}$

(ii) $X^{+} \rightarrow X^{2+} + e^{-}$

(e) How do the values of successive ionisation energies of an element provide evidence for the existence of energy levels?

(f) What name is given to the energy change represented by $X^{2+} \rightarrow X^{3+} + e^{-}$?

7.4 **(a)** The variation of first ionisation energy with atomic number for six successive elements is shown in Figure 7.20. Give reasons for the general increase indicated and explain why the increase is interrupted at one point. [LCH]

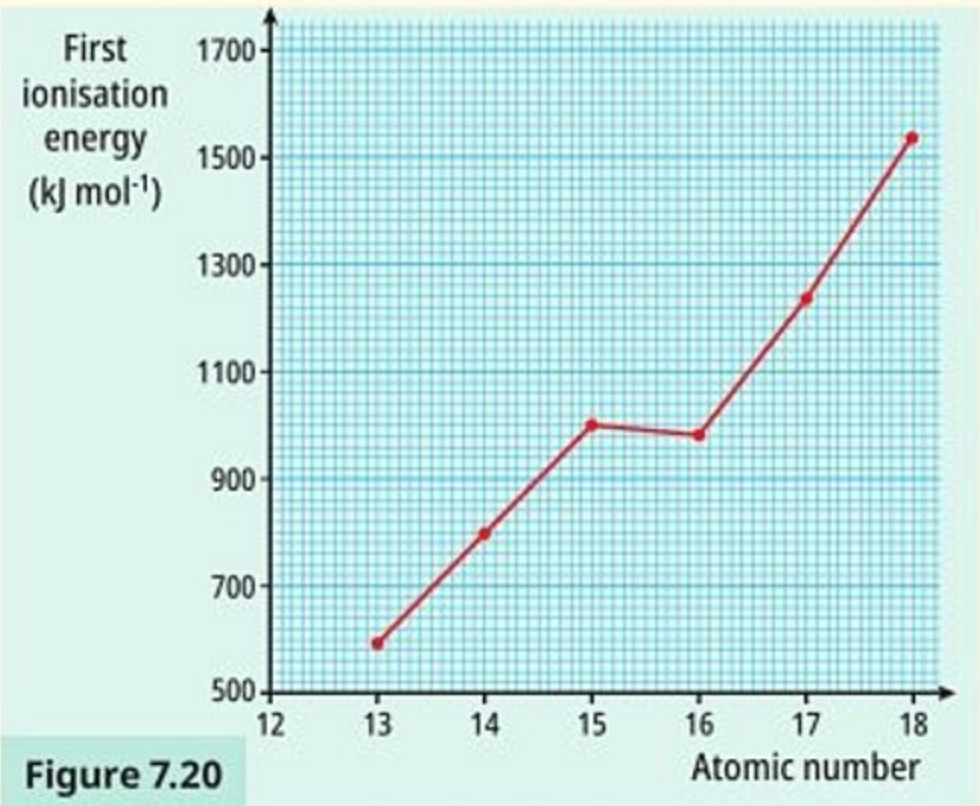


Figure 7.20

(b) Discuss, with suitable explanations, how the following properties vary across a typical period (e.g. Na to Ar) of the Periodic Table:

(i) Atomic radius

(ii) First ionisation energy. [LCH]

7.5 **(a)** What is meant by the *first ionisation* energy of an element?

Explain:

(i) The decrease in first ionisation energies down a group of the Periodic Table, e.g. Be to Ba

(ii) The increase in electronegativity values across a period of the Periodic Table, e.g. Li to F.

(b) The first and second ionisation energies of sodium and magnesium are shown in Table 7.4. Explain why sodium has a lower first ionisation energy but a much higher second ionisation energy than magnesium. [LCH]

Ionisation energy	Na	Mg
First	494	736
Second	4550	1450

Table 7.4

Chapter review questions

7.6

(a) What is meant by electronegativity?

(b) How are the electronegativities of elements related in general to their position in the Periodic Table? Give reasons in support of your answer. [LCH]

(c) How does the reactivity of the alkali metals vary moving down the group?

(d) Explain what happens to the reactivity of the halogens moving down the group.

(e) What is observed if chlorine gas is bubbled into a solution containing bromide ions?

(f) How do the boiling points of the noble gases vary down the group?

(g) Which one of the halogens is a solid at room temperature?

7.7 Some crystals of a certain halogen were placed in a conical flask. A test-tube containing ice was clamped in the conical as shown in Figure 7.21. The conical flask was gently warmed.

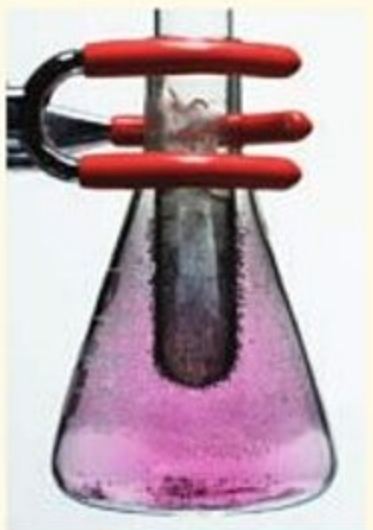


Figure 7.21

(a) Name the halogen shown in Figure 7.21.

(b) On heating, it was observed that the crystals did not melt to a liquid but changed directly into a vapour. What is this process called?

(c) After heating the crystals in the conical flask, crystals were also seen to form on the test-tube. Explain this observation.

(d) What is the purpose of putting ice in the test-tube?

(e) Describe what happens at the molecular level when the crystals are gently heated and change from solid to gas.

(f) Identify the main type of intermolecular force present between the molecules in the crystal structure of the crystals being heated.

(g) Explain how the forces identified in (f) arise.

(h) Predict how the melting point of the purple crystals would compare with that of crystals of sodium chloride. Justify your prediction.

7.8

(a) Why do alkali metals have similar chemical properties?

(b) Why are alkali metals stored under oil?

(c) Why do alkali metals not occur freely in nature?

(d) What common name is given to calcium carbonate?

(e) Which alkaline earth metal reacts slowly with cold water but vigorously with steam?

(f) Which halogen is the most electronegative element in the Periodic Table?

(g) What do you observe when chlorine is bubbled through a solution containing bromide ions?

(h) Why do the boiling points of noble gases increase down the group?

(i) Explain why elements in Group 1 show similar chemical behaviour.

(j) Describe the trend in reactivity of alkali metals with water as you move down the group.

(k) Describe how the low ionisation energy of alkali metals affects their reactivity.

(l) Describe what is observed when sodium is cut with a knife.

(m) Explain why the reactions of rubidium and caesium with water are not demonstrated in school laboratories.

(n) Describe how the atomic radius and screening effect influence ionisation energies.

(o) Explain why halogens are described as 'salt producers'.

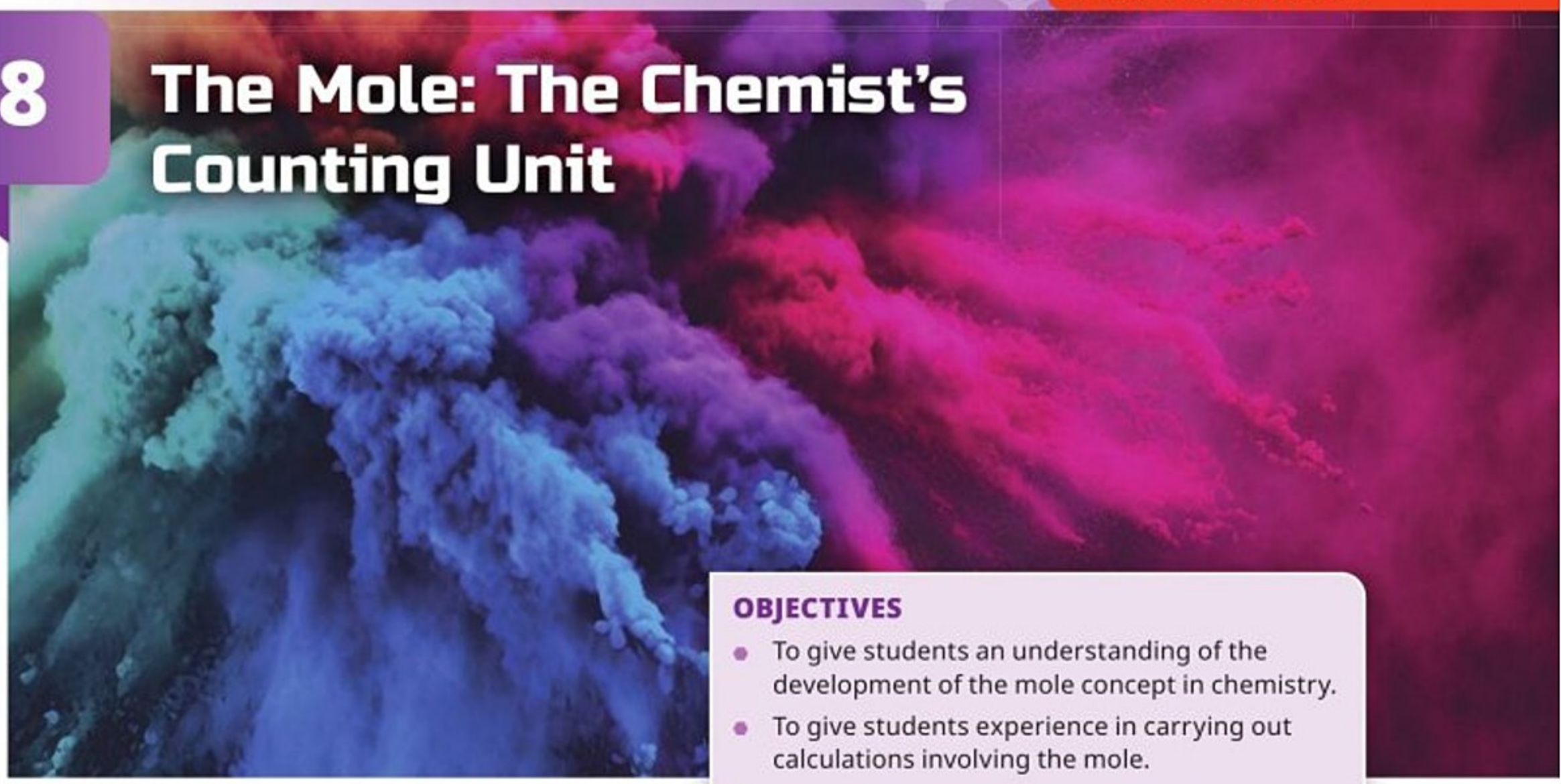
(p) Describe the physical states of chlorine, bromine, and iodine at room temperature.

(q) Explain the process of sublimation using iodine as an example.

(r) Describe what happens when bromine water is added to a solution of iodide ions.

(s) Explain why the reactivity of halogens increases up the group, unlike the alkali metals.

8 The Mole: The Chemist's Counting Unit

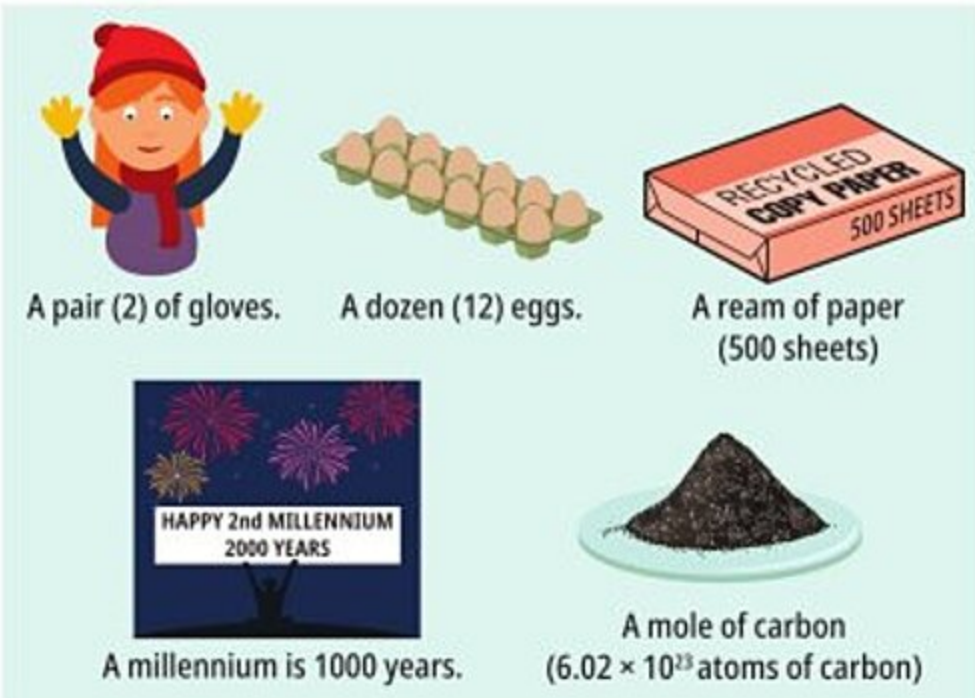


OBJECTIVES

- To give students an understanding of the development of the mole concept in chemistry.
- To give students experience in carrying out calculations involving the mole.
- To make students familiar with the applications of the mole concept in chemistry.

8.1 Introduction

In our everyday lives, we use various counting units, e.g. a pair (2) of gloves, a dozen (12) of eggs, a ream of writing paper (500 sheets) and a millennium (1,000 years), Figure 8.1. When studying chemistry, we deal with very tiny particles such as atoms, molecules and ions. It would not be possible to count these individually because even a small sample of a substance contains very large numbers of these tiny particles. Therefore, to help us count these tiny particles, which are invisible to the naked eye, chemists have invented a special counting unit called the **mole**.



A pair (2) of gloves. A dozen (12) eggs. A ream of paper (500 sheets)

A millennium is 1000 years. A mole of carbon (6.02×10^{23} atoms of carbon)

Figure 8.1 Some examples of counting units. The mole is the counting unit used by chemists.

Just as the kilogram is the SI unit of mass, the mole is the SI unit of **amount** of substance. The symbol for the mole is **mol**.

In 2018 the International Union of Pure and Applied Chemistry (IUPAC) defined a mole as follows:

One **mole** of a substance contains 6.02×10^{23} elementary entities of the substance.

- The word 'entity' simply means something that exists as its own single and separate unit. Examples of 'elementary entities' in chemistry are atoms, molecules and ions.
- When referring to a mole of anything, the elementary unit should always be specified. For example, the phrase 'one mole of chlorine' should never be used. We should specify the elementary unit, e.g. one mole of chlorine atoms, or one mole of chlorine molecules, or one mole of chloride ions.
- The number 6.02×10^{23} is called the **Avogadro constant**. The symbol for the Avogadro constant is N_A.
- The Avogadro constant is named in honour of a famous Italian chemist called Amedeo Avogadro, who devised a method for chemists to count atoms and molecules, Figure 8.2. The Avogadro constant is determined by experiment using X-rays and also by passing fixed quantities of electrical charges through chemical solutions. The value is known precisely and is defined by IUPAC as $6.02214076 \times 10^{23}$. When using this number in calculations, we usually use 6.02×10^{23}.

- It is found by experiment that 12 grams of the carbon-12 isotope contain 6.02×10^{23} atoms of carbon. This is shown diagrammatically in Figure 8.3.

NOTE

The number 6.02×10^{23} is an enormous number and is difficult to comprehend because it is beyond our everyday experiences. It is greater than the entire population of the Earth and greater than the number of grains of sand on the Earth.

Avogadro's ideas may be summarised as follows:

- We know from our study of the Periodic Table that an atom of magnesium is twice as heavy as an atom of carbon: relative atomic mass (A_r) of Mg = 24, relative atomic mass of C = 12, Figure 8.4
- Since one atom of magnesium is twice as heavy as one atom of carbon, then one hundred magnesium atoms are twice as heavy as one hundred carbon atoms. Similarly, a million magnesium atoms are twice as heavy as a million carbon atoms.
- Therefore, if we have a piece of magnesium that has twice the mass of a piece of carbon, the two amounts must contain equal numbers of atoms. Think carefully about this. For example, 2 grams of magnesium and 1 gram of carbon contain the same number of atoms. Similarly, 20 kilograms of magnesium and 10 kilograms of carbon contain the same number of atoms.
- Let's look at carbon and hydrogen as a further example. Since an atom of carbon (A_r = 12) has a mass 12 times that of an atom of hydrogen (A_r = 1), 1 gram of hydrogen atoms and 12 grams of carbon atoms both contain the same number of atoms.
- Similarly, if we look at silver and carbon, a silver atom (A_r = 108) has nine times the mass of a carbon atom (A_r = 12). Therefore, if we have 12 g of carbon, this will contain a certain number of atoms. To calculate the mass of silver which will contain the same number of atoms of carbon, it is $9 \times 12 = 108$ g.

In short, **if we weigh out elements in the same proportions as their relative atomic masses (A_r), we will always have the same number of atoms of these elements**. Therefore, a chemist can 'count the number of atoms by weighing'. This is similar to the way that a bank cashier can count the number of coins in a bag by weighing the bag.

Figure 8.2

Amedeo Avogadro
(1776–1856)

Amedeo Avogadro was an Italian chemist who set up a system to enable chemists to count atoms and molecules.

Figure 8.3 It is found that 12 grams of the carbon-12 isotope contains 6.02×10^{23} atoms of carbon. In other words, a mole of carbon is 12 grams.

Figure 8.4 An atom of magnesium is twice as heavy as an atom of carbon.

Suppose we take the relative atomic mass in grams of a number of elements, Table 8.1.

Element	Mass
Carbon	12 g
Magnesium	24 g
Aluminium	27 g
Calcium	40 g
Iron	56 g
Copper	63.5 g
Silver	108 g

Table 8.1 All these different masses of elements contain the same number of atoms.

Table 8.1 is illustrated in Figure 8.5.

Figure 8.5 The amount of each element (1 mole) contains the same number (6.02×10^{23}) atoms.

All the amounts of each element listed in Table 8.1 contain the same number of atoms, i.e. 6.02×10^{23}. The Avogadro constant is also called **Avogadro's number**. The 'old' definition of the mole was that it is the number of atoms of carbon in 12 g of the carbon-12 isotope. However, the new definition given above was agreed by IUPAC in 2018 in order to put the emphasis on the Avogadro constant.

The word 'mole' comes from the Latin word *moles* meaning 'a heap or pile'. It draws attention to the particle nature of matter – a heap or pile of particles containing the Avogadro constant number of particles.

NOTE

Chemistry students all over the world celebrate National Mole Day which begins at 6:02 a.m. on 23 October each year, Figure 8.6. You will find lots of information online about this event and also lots of really great mole jokes, such as:

Q. What face cream did Avogadro invent?

A. Oil of Molay.

Q. What element do moles love to study in chemistry?

A. Molybdenum.

Q. How did Avogadro help his team win the match?

A. He scored the winning Mole.

Q. What did Avogadro have on his pancakes?

A. Molasses.

Q. What did the chemistry teacher say when she saw all of her students in the lab at 6:02 a.m.?

A. 'Holy Moley, there's a Mole-titude of students here!'

Q. How do you contact a mole?

A. Call Avogadro's number.

Enough jokes – let's get back to work!

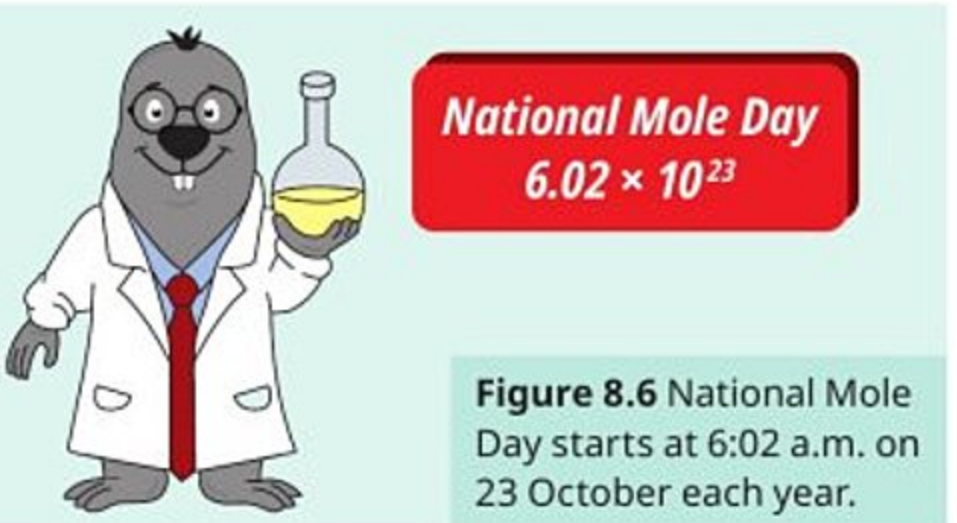


Figure 8.6 National Mole Day starts at 6:02 a.m. on 23 October each year.

Thus, when you weigh out 12 g of carbon, this amount of carbon contains 6.02×10^{23} atoms of carbon. We say that this **amount** of carbon is one mole (1 mol) of carbon atoms. Similarly, 48 g of magnesium is two moles (2 mol) of magnesium atoms. We say that the **amount** of magnesium is two moles (2 mol). The mole concept is a very useful one for chemists, as it enables them to calculate the number of atoms (or molecules or ions) that are in a particular amount of a substance that they have weighed out.

We will now learn how to carry out various calculations involving the mole. These calculations are:

1. How to convert moles to grams.
2. How to convert grams to moles.
3. How to perform calculations involving the Avogadro Constant.
4. How to perform miscellaneous calculations from past exam papers.

8.2 How to convert moles to grams

Hopefully, it is clear from Section 8.1 that the mass of one mole of any element is simply the relative atomic mass expressed in grams.

Mass of **one mole of an element** = Relative Atomic Mass in grams.

Table 8.2 lists the relative atomic masses of some common elements.

Element	Symbol	Relative Atomic Mass
Hydrogen	H	1.008
Carbon	C	12.01
Nitrogen	N	14.01
Oxygen	O	16.00
Sodium	Na	22.99
Chlorine	Cl	35.45

Table 8.2 The relative atomic masses of some common elements

From Table 8.2, it is clear that one mole of Na = 22.99 grams, one mole of O_2 (oxygen molecules) = 32.00 grams, etc.

For all calculations involving the mole concept, you will need to refer to a list of relative atomic masses of elements. A list of the relative atomic mass values needed for calculations is included in *Formulae and Tables* booklet published by the State Examinations Commission. Read carefully the instructions on exam papers, as you may be told to round off the relative atomic masses.

Example 8.1

Question

Aluminium metal is very useful in construction, Figure 8.7. What is the mass of three moles of aluminium atoms?

Figure 8.7

Answer

1 mole of Al = 26.98 g

3 moles of Al = 26.98 × 3

= 80.94 g Answer: 80.94 grams.

If we add up the relative atomic masses of all the atoms in a molecule of a compound, we obtain what is called the **relative molecular mass (M_r)** of the compound. **The relative molecular mass of a compound is the sum of the relative atomic masses of all the atoms in a molecule of the compound**.

The **relative molecular mass** of a compound is the average mass of one molecule of that compound compared with one-twelfth of the mass of one atom of the carbon-12 isotope.

The definition of relative molecular mass that you should use in exams is:

Relative molecular mass is sometimes referred to as **relative formula mass**. This is because some compounds (e.g. NaCl) consist of ions rather than molecules. However, in this textbook, we will use the term *relative molecular mass*, as this term is more widely used and is the term specified on the syllabus.

The method of calculating the relative molecular mass of a compound is shown in Example 8.2.

Example 8.2

Question

What is the relative molecular mass of water, H_2O?

Answer

Rel. atomic mass of 2 H = 2 × 1.008 = 2.016
Rel. atomic mass of 1 O = 1 × 16.00 = 16.00
Relative molecular mass = 18.016

Thus, we may conclude that one mole of H_2O = 18.016 grams.
In this amount of water there are 6.02×10^{23} molecules of water.

Answer: 18.016

From this example it is clear that:

Mass of **one mole of a compound** = Relative Molecular Mass in grams.

In Chapter 4, we saw that the mass spectrometer may be used to measure relative atomic masses and abundances of isotopes. A second important use of the mass spectrometer is to measure relative molecular masses. The molecule is broken up into ions in the mass spectrometer and, from a study of the fragments that are formed, chemists can determine the relative molecular mass of the substance.

Molar mass

The mass of one mole of a substance is often referred to as the **molar mass**, e.g. the molar mass of carbon is 12 g mol^{-1}. Thus, the molar mass of an element is the relative atomic mass expressed in grams per mole.

The molar mass is the atomic mass or the molecular mass of the substance expressed in grams. Some examples of molar masses are listed in Table 8.3.

The **molar mass** is the mass of one mole of any substance (element or compound) expressed in grams per mole (g mol^{-1}).

Substance (element or compound)	Molar mass (g mol^{-1})	Number of particles	Type of particles
Na	22.99	6.02×10^{23}	Atoms
O_2	32.00	6.02×10^{23}	Molecules
H_2O	18.02	6.02×10^{23}	Molecules
NaCl	58.44	6.02×10^{23}	Formula units

Table 8.3 Some examples of molar masses

Molar masses of some compounds are shown in Figure 8.8.

Note also that molar mass has units of grams per mole (g mol^{-1}). Since 1 mole of water has a mass of 18.02 grams, this means that the molar mass of water is 18.02 g mol^{-1}. However, the relative molecular mass of water is simply written as 18.02. There are no units since relative molecular mass (and relative atomic mass) compare masses relative to one-twelfth of the mass of the carbon-12 isotope. Therefore, the units cancel out.

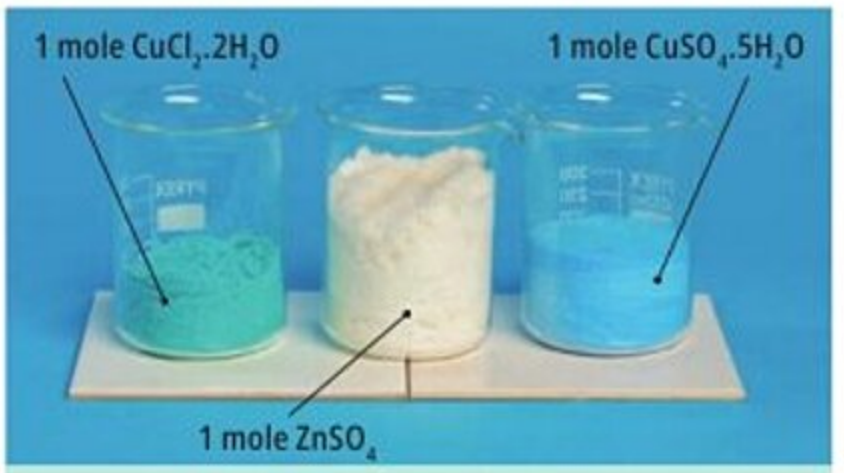


Figure 8.8 The amount of each compound (1 mole) is called the molar mass and contains the same number (6.02×10^{23}) of entities (atoms, molecules or formula units).

Example 8.3

Question

Aluminium sulfate contains sulfate ions, Figure 8.9. What is the mass of one mole of sulfate ions, SO_4^{2-}?

Answer

1 S = 1 × 32.07	= 32.07
4 O = 4 × 16.00	= 64.00
Rel. Molecular Mass	= 96.07

i.e. one mole of sulfate ions = 96.07 grams

Answer: 96.07 g

Figure 8.9

NOTE

The negative charges make no difference to the calculations (since electrons have negligible mass).

Example 8.4

Question

Copper(II) sulfate is commonly used to control fungal diseases in trees, Figure 8.10.
What is the mass of one mole of hydrated copper(II) sulfate, $CuSO_4.5H_2O$?

Answer

Cu	= 63.5
S	= 32.07
4 O= 4 × 16.00	= 64.00
H_2O= 5 × 18.016	= 90.08
Rel. Molecular Mass	= 249.65

i.e. one mole of $CuSO_4.5H_2O$ = 249.65 grams.
$CuSO_4.5H_2O$ has a relative molecular mass of 249.65.

Answer: 249.65 g

Figure 8.10 Copper sulfate is being used to control fungal growth on this apple tree.

Example 8.5

Question

Calculate the mass of 0.125 mole of calcium chloride, $CaCl_2$.

Answer

Ca	= 40.08
2 Cl = 2 × 35.45	= 70.9
Rel. Molecular Mass	= 110.98

i.e. one mole $CaCl_2$ = 110.98 g.
Therefore, 0.125 moles $CaCl_2$ = 110.98 × 0.125
= 13.8725 g

Answer: 13.8725 g

From Example 8.5 we see a very useful relationship:

Mass (in grams) = Relative molecular mass × Number of moles

We have now completed the first type of calculation on how to convert moles to grams. So let's see how well you can perform on this type of calculation!

TEST YOURSELF:
Attempt Questions 8.1–8.3 and W8.1–W8.3.

8.3 How to convert grams to moles

In the previous section, we learned how to convert moles to grams. In the second type of calculation, we will learn how to do the reverse, i.e. convert grams to moles.

Example 8.6

Question

The 'lead' in pencils consists of a pure form of carbon called graphite, Figure 8.11.
How many moles are there in 36.02 g of the element carbon?

Answer

12.01 g carbon = 1 mole

Therefore, 1 g carbon $= \frac{1}{12.01}$ mole

Therefore, 36.02 g carbon $= \frac{36.02}{12.01}$ mole

$= 2.999$ moles.

Answer: 2.999 moles

Figure 8.11 Graphite is a form of the element carbon that is found in pencils.

From the above example, it is clear that:

$$\text{No. of moles of an element} = \frac{\text{Mass of element}}{\text{relative atomic mass}}$$

In the case of elements that consist of two atoms (e.g. H_2, O_2, N_2), use the relative molecular mass instead of relative atomic mass when performing calculations using the above equation.

Similarly, if one is dealing with a compound, the relationship becomes:

$$\text{No. of moles of a compound} = \frac{\text{Mass of compound}}{\text{relative molecular mass}}$$

This type of calculation is shown in Example 8.7.

Example 8.7

Question

How many moles of water molecules are there in 117 g of water?

Answer

First calculate the relative molecular mass of water

O = 16.00

2 H = 2 × 1.008 = 2.016

Rel. Molecular Mass = 18.016

Number of moles of water $= \frac{\text{Mass of water}}{\text{Rel. molecular mass of water}} = \frac{117}{18.016} = 6.49$ moles

Answer: 6.49 moles

We can summarise the above two relationships in the following general relationship:

$$\text{Number of moles of a substance} = \frac{\text{Mass of the substance}}{\text{Mass of one mole of the substance}}$$

Example 8.8

Question

How many moles of sulfuric acid, H_2SO_4, are there in 12.25 g of sulfuric acid?

Answer

First calculate the relative molecular mass of sulfuric acid, H_2SO_4

2 H = 2 × 1 .008	= 2.016
1 S = 1 × 32.07	= 32.07
4 O = 4 × 16.00	= 64.00
Rel. Molecular Mass	= 98.086

No. of moles of H_2SO_4

$$= \frac{\text{Mass of } H_2SO_4}{\text{Mass of one mole of } H_2SO_4} = \frac{12.25}{98.086} = 0.125 \text{ mole}$$

Answer: 0.125 mol

In solving problems involves mass, number of moles and relative molecular mass, some students may find it helpful to use the 'mole triangle' that relates the above three variables, as shown in Figure 8.12. Place your thumb over the variable that you wish to calculate and you will see what must be done with the other two variables in order to solve the problem.

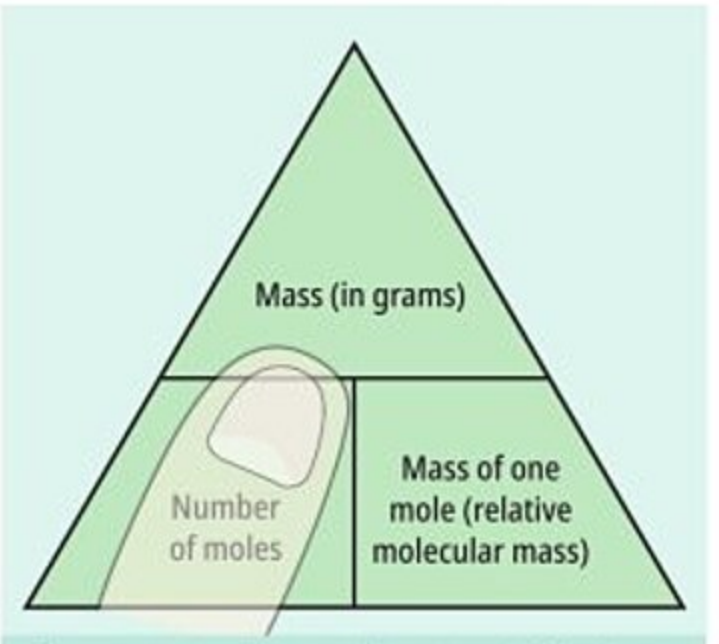


Figure 8.12 The mole triangle helps to relate the number of moles, the mass (in grams) and the mass of one mole (molar mass or relative molecular mass).

8.4 How to perform calculations involving the Avogadro constant

Calculations involving Avogadro's number may be divided into four types. All calculations are based on the following fact:

One **mole** of a substance contains **6.02×10^{23}** particles of that substance.

The following examples indicate the type of calculations involved.

(a) Converting moles to number of atoms or molecules

TEST YOURSELF: Attempt Questions 8.4–8.5 and W8.4–W8.5.

Example 8.9

Question

How many atoms of sodium are present in 0.25 mole of this metal, Figure 8.13?

Answer

1 mole of sodium contains 6.02×10^{23} atoms.

$\therefore$ 0.25 mole of sodium contains $0.25 \times 6.02 \times 10^{23}$ atoms

$= 1.505 \times 10^{23}$ atoms

Answer: 1.505×10^{23} atoms

Figure 8.13 Calculating the number of atoms of sodium present

» Study Example 8.10 in the online resources.

(b) Converting grams to number of atoms or molecules

Example 8.11

Question

How many atoms are there in 28.75 g of sodium?

Answer

1 mole of sodium contains 6.02×10^{23} atoms,

i.e. 22.99 g sodium contains 6.02×10^{23} atoms

Therefore, 1 g sodium contains $\frac{6.02 \times 10^{23}}{22.99}$

Therefore, 28.75 g sodium contains $\frac{28.75 \times 6.02 \times 10^{23}}{22.99}$ atoms $= 7.528 \times 10^{23}$ atoms

Answer: 7.528×10^{23} atoms

Example 8.12

Question

Carbon dioxide is commonly used in fire extinguishers, Figure 8.15. How many molecules of carbon dioxide are there in a fire extinguisher which contains 150 g of carbon dioxide?

Answer

First calculate the relative molecular mass of CO_2

1 C = 1 × 12 .01 = 12.01
2 O = 2 × 16.00 = 32.00
Rel. Molecular Mass = 44.01

1 mole of CO_2 contains 6.02×10^{23} molecules

i.e. 44.01 g CO_2 contain 6.02×10^{23} molecules

1 g CO_2 contains $\frac{6.02 \times 10^{23}}{44.01}$ molecules

150 g CO_2 contains $\frac{150 \times 6.02 \times 10^{23}}{44.01}$ molecules

$= 2.05 \times 10^{24}$ molecules

Figure 8.15 Calculate the number of carbon dioxide molecules that was in the fire extinguisher.

Answer: 2.05×10^{24} molecules

(c) Converting numbers of atoms or molecules to moles

Example 8.13

Question

How many moles of aluminium atoms are there in 9×10^{22} atoms of aluminium?

Answer

6.02×10^{23} atoms of Al = 1 mole

1 atom of Al = $\frac{1}{6.02 \times 10^{23}}$ mole

9×10^{22} atoms of Al = $\frac{9 \times 10^{22}}{6.02 \times 10^{23}}$ mole

= 0.15 mole

Answer: 0.15 mol

(d) Converting numbers of atoms or molecules to grams

Example 8.14

Question

How many grams of zinc are present in 3×10^{20} atoms of zinc?

Answer

1 mole of Zn has a mass of 65.41 grams,

i.e. 6.02×10^{23} atoms of zinc have a mass of 65.41 g

1 atom of zinc has a mass of $\frac{65.41}{6.02 \times 10^{23}}$ g

3×10^{20} atoms have a mass of $\frac{3 \times 10^{20} \times 65.41}{6.02 \times 10^{23}}$ g

$= 0.0326$ g

Answer: 0.0326 g

Example 8.15

Question

What is the mass (in grams) of 3×10^{22} molecules of ethanol, C_2H_5OH?

Answer

First calculate the relative molecular mass of ethanol

2 C = 2 × 12 .01	= 24.02
5 H = 5 × 1.008	= 5.04
1 O = 1 × 16.00	= 16.00
1 H = 1 × 1.008	= 1.008
Rel. Molecular Mass	= 46.068

i.e. 1 mole of C_2H_5OH = 46.068 g

$\therefore$ 6.02×10^{23} molecules of C_2H_5OH = 46.068 g

1 molecule of $C_2H_5OH = \frac{46.068}{6.02 \times 10^{23}}$ g

3×10^{22} molecules of C_2H_5OH

$= \frac{3 \times 10^{22} \times 46.068}{6.02 \times 10^{23}}$

$= 2.296$ g

Answer: 2.296 g

TEST YOURSELF: Attempt Questions 8.6–8.8 and W8.6–W8.9.

8.5 Miscellaneous questions

In the Leaving Certificate exam paper, there may be some short questions on the mole concept.

Study Examples 8.16–8.18 in the online resources.

8.6 Some concluding points

It is very important that you have a good understanding of the mole. It is one of the key concepts in chemistry and you will be meeting it frequently in subsequent chapters. As you will have seen from the above examples, many questions on the mole can be answered if you remember two important facts.

$$\text{Number of moles} = \frac{\text{Mass in grams}}{\text{Relative molecular mass}}$$

One mole of any substance contains 6.02×10^{23} entities.

Summary What I should know

- The mole concept was introduced in order to enable us to calculate the number of atoms (or molecules or ions) in a particular amount of substance we have weighed out.
- One **mole** of a substance contains 6.02×10^{23} elementary entities of the substance.
- The relative molecular mass of a compound is the mass of one molecule of that compound compared with one twelfth of the mass of one atom of the carbon-12 isotope.
- The mass of one mole of an element is the relative atomic mass in grams.
- The mass of one mole of a compound is the relative molecular mass in grams.
- The **molar mass** is the mass of one mole of any substance (element or compound) expressed in grams per mole ($g\ mol^{-1}$).
- Number of moles of a substance = $\frac{\text{Mass of the substance}}{\text{Mass of one mole of the substance}}$
- Calculations involving Avogadro's number are based on the fact that one mole of a substance contains 6.02×10^{23} particles of that substance.

Learning outcomes

At the end of this chapter, I should be able to:

Explain the concept of the mole and the Avogadro constant.	⬡	⬡	⬡
Perform calculations to convert moles to grams.	⬡	⬡	⬡
Discuss the concept of molar mass.	⬡	⬡	⬡
Perform calculations to convert grams to moles.	⬡	⬡	⬡
Perform calculations involving the Avogadro constant.	⬡	⬡	⬡

Chapter review questions

8.1 A sulfur atom weighs twice as much as an oxygen atom. If a chemist has 16.02 grams of oxygen atoms, how many grams of sulfur would contain the same number of atoms as in the sample of oxygen atoms?

8.2 **(a)** What is meant by *one mole* of a substance? [LCH]

(b) What is the mass of one mole of each of the following substances

(i) hydrogen molecules
(ii) nitrogen molecules
(iii) oxygen molecules
(iv) chlorine molecules
(v) fluorine molecules
(vi) bromine molecules?

8.3 Calculate the relative molecular mass of each of the following substances

(a) sulfuric acid, H_2SO_4
(b) carbon dioxide, CO_2
(c) hydrogen iodide, HI
(d) sodium chloride, NaCl
(e) aluminium bromide, $AlBr_3$
(f) sulfur dioxide, SO_2
(g) copper(II) carbonate, $CuCO_3$
(h) sodium carbonate, Na_2CO_3
(i) sodium hydroxide, NaOH
(j) nitrate ion, NO_3^-
(k) hydrated sodium carbonate, $Na_2CO_3.10H_2O$
(l) calcium phosphate $Ca_3(PO_4)_2$
(m) hydrated iron(II) sulfate, $FeSO_4.7H_2O$
(n) table sugar, $C_{12}H_{22}O_{11}$

8.4 Calculate the number of moles of each element in

(a) 69 g sodium
(b) 162.5 g zinc
(c) 6.5 g chromium
(d) 254 g copper
(e) 31.05 g lead.

8.5 Calculate the number of moles in

(a) 192 g O_2
(b) 4 g Br_2
(c) 140 g N_2
(d) 56.02 g CO
(e) 0.7 g C_2H_4
(f) 9.6 g sulfate ion, SO_4^{2-}

8.6 How many atoms are present in

(a) 0.54 moles carbon
(b) 1.24 moles tin
(c) 6.2 moles zinc
(d) 200 moles iron
(e) 5×10^{-5} moles silver?

8.7 How many atoms are present in

(a) 54 g aluminium
(b) 168 g silver
(c) 96.02 g magnesium
(d) 3.36 g iron
(e) 0.12 g carbon

8.8 How many moles of atoms are present in

(a) 5×10^{24} atoms of carbon
(b) 8×10^{2} atoms of zinc
(c) $2.6.02 \times 10^{12}$ atoms of gold
(d) 9.8×10^{27} atoms of silver
(e) 1.3×10^{6} atoms of magnesium

9 Kinetic Theory of Matter and Behaviour of Gases

OBJECTIVES

- To give students an understanding of the evidence for the Kinetic Theory of Matter.
- To ensure that students appreciate the relationships between pressure, volume and temperature of gases.
- To provide students with the opportunity to carry out an experiment to determine the relative molecular mass of a gas in the school laboratory.
- To ensure that students know how to solve problems involving the behaviour of gases.

9.1 Introduction

You may recall in Chapter 2 that we learned that the word 'matter' is simply a scientific term for substances or materials. A more formal definition of matter is as follows:

Matter is anything that takes up space and has mass.

We also learned that the fact that materials are made up of small particles is often referred to as the **particulate nature of matter**. By 'particles' we mean tiny entities that are invisible to the naked eye, e.g. atoms, molecules and ions. In pure substances (elements and compounds) all the particles in any one particular element or compound are the same. Figure 9.1 (a) and (b).

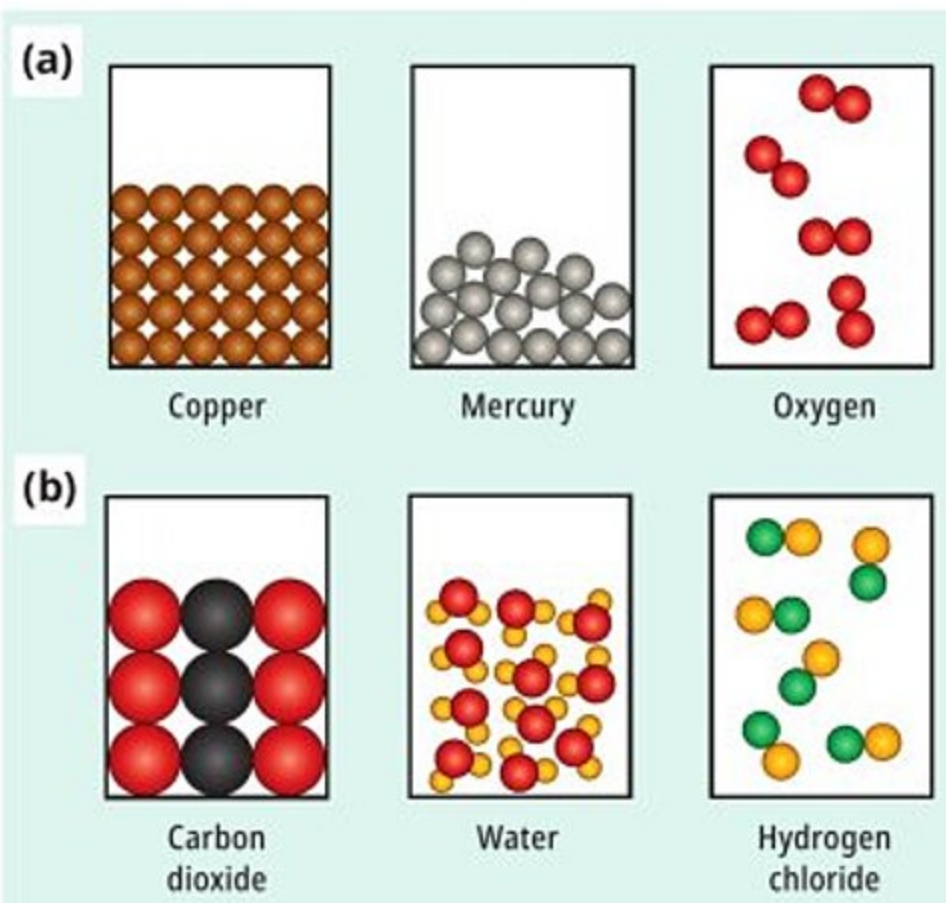


Figure 9.1 Particles in pure substances: (a) elements and (b) compounds.

In a mixture of substances (e.g. oxygen gas and hydrogen gas), then the particles in the mixture will not be the same. In a mixture, different particles are mingled together (in this case, a mixture of oxygen molecules and hydrogen molecules).

In Chapter 2, we studied one property of a gas, i.e. its ability to spread throughout all the available space. We saw that ammonia gas and hydrogen chloride gas spread from opposite ends of a glass tube and formed a white ring where they met, Figure 2.1 (p.9). It is found that a gas will spread throughout any container in which it is placed. This spreading of gases is called **diffusion**. For example, if a small amount of a gaseous air freshener is released into a room, it will be detected in all parts of the room after a short time. Similarly, smoke can quickly spread throughout a building due to diffusion.

If some crystals of iodine are heated, they change directly from a solid to a gas (**sublimation**), Figure 9.2 Note that the gaseous iodine fills the entire container.

Figure 9.2 When iodine crystals are warmed, the iodine gas that is formed fills the entire flask.

In this chapter, we will study the laws that gases obey and we will learn why they obey these laws. Before we study these laws, we first study a theory which helps us to understand the behaviour of gases.

9.2 The Kinetic Theory of Matter

Many of the ideas about the behaviour of atoms, molecules and ions in solids, liquids and gases are summarised in a theory called the Kinetic Theory of Matter. The word 'kinetic' comes from a Greek word meaning 'movement'. You may recall that at Junior Cycle, this theory was called the 'particle theory'. As we are going to study this theory in more detail, the term *Kinetic Theory* will be used.

The main points of the Kinetic Theory of Matter can be summarised in a number of assumptions.

Assumptions of the Kinetic Theory of Matter

1. **All matter is made up of tiny particles that are invisible to the naked eye.** In this course, the tiny particles that we will be studying will be mainly atoms and molecules.
2. **The tiny particles are always in motion.** The degree of motion depends on whether the substance is a solid, liquid or gas. These three are often referred to as the three **states of matter.**

- In **solids**, the particles are packed closely together. They do not have as much energy as particles in the liquid and gaseous states. The particles can only vibrate about fixed positions, Figure 9.3(a) in Table 9.1.
- In **liquids**, the particles are also packed closely together but are not in fixed positions as they are in solids. Evidence for this is the fact that liquids cannot be compressed, Figure 9.3(b).
- In **gases**, the particles are more widely separated and have larger amounts of energy than the particles in solids and liquids. The energy of gas particles is sufficient to spread out and fill the container, Figure 9.3(c). Gas particles move very fast in a random and haphazard way. The particles of a gas have more freedom of movement than the particles of a solid or a liquid.

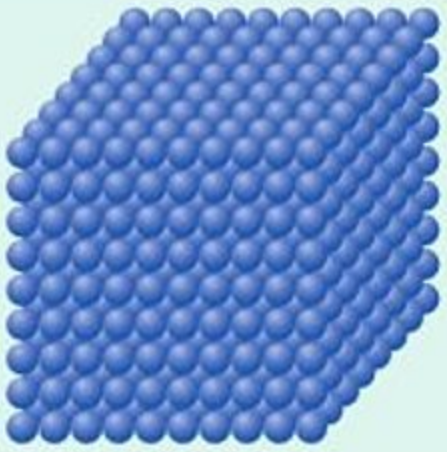
Solid	Liquid	Gas
 **Figure 9.3(a)** The arrangement of particles in a solid	**Figure 9.3(b)** The arrangement of particles in a liquid	**Figure 9.3(c)** The arrangement of particles in a gas
• The particles (atoms, molecules, ions) are in fixed positions and do not move about but can vibrate. • The particles are packed closely together • Strong forces hold the particles together.	• The particles have more freedom of movement than in a solid. • The particles are very close together. • The particles in the liquid can slide over each other. • The forces between the particles are not as strong as in a solid.	• The particles in a gas are farther apart than in a solid or liquid. • The particles are continuously moving very fast around in all the space available. • The movement is random and haphazard. The particles collide with each other and with the walls of the container. • There are weak forces between the particles.

Table 9.1 Summary of some key points in the Kinetic Theory of Matter

3. Temperature affects the movement of particles.

- An increase in temperature causes an increase in the kinetic energy of the particles, i.e. the particles move faster. Kinetic energy is energy due to movement.
- A decrease in temperature (reduced energy) causes a decrease in the kinetic energy of the particles, i.e. the particles move more slowly.

4. Temperature can cause a change in state.

When a solid is heated, the heat energy causes the vibration of the particles to increase. As heating continues, the particles vibrate faster and faster. The more heat that is supplied, the more the particles vibrate. Eventually, the particles break free and begin to slide over each other. The solid has now melted to form a liquid. We say that a change of state has occurred.

The **melting point** is the temperature at which a solid changes to a liquid.

A small number of solids change directly from a solid to a gas when heated. This occurrence is known as **sublimation**. Solid carbon dioxide ('dry ice') and iodine are examples of substances that sublime. Dry ice is often used in special effects, Figure 9.4.

Figure 9.4 Solid carbon dioxide changes directly from a solid to a gas. This process is called sublimation and is used in special effects.

You may have noticed that puddles on the road dry up quickly on a warm, sunny day. This is because heat from the Sun gives some particles **near the surface** of the liquid extra energy. These particles now have enough energy to escape from the liquid into the air. We say that some of the liquid has **evaporated** to form a gas.

Evaporation is the changing of a liquid to a gas at the surface of the liquid.

When a liquid is heated, the particles obtain more energy and move faster and faster. Eventually, the particles break away from the liquid state and form a gas. When a certain temperature is reached, particles of gas form throughout the liquid and not just at the surface. The liquid is now boiling.

When a liquid is boiling, the particles are escaping from all parts of the liquid very quickly.

Bubbles of gas are seen forming **throughout the liquid**. In the case of water, these bubbles of gas are made up of water vapour. The boiling point of the liquid has then been reached, Figure 9.5.

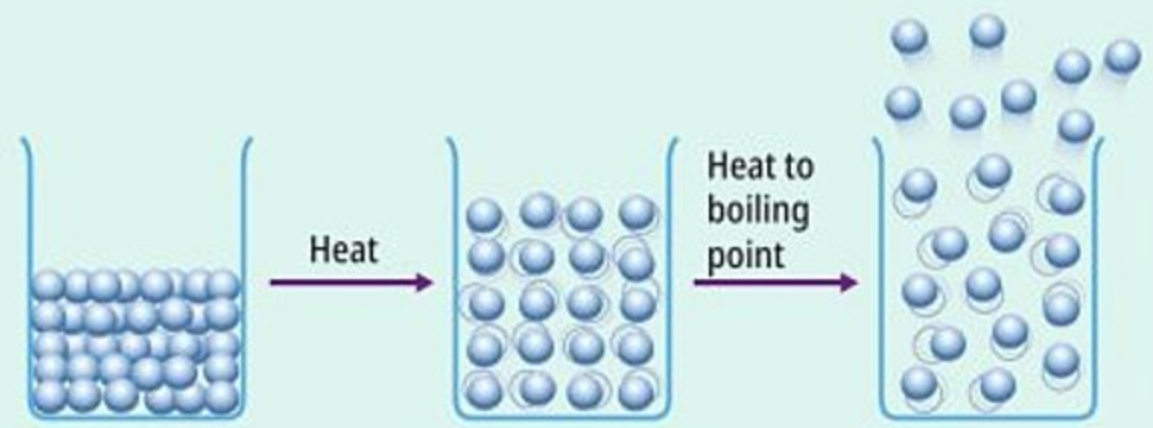

Heat
Heat to boiling point
Particles in liquid
Particles move faster
Liquid boiling – particles have enough energy to escape

Figure 9.5 At the boiling point of a liquid, the particles break away from all parts of the liquid and form a gas.

The **boiling point** of a liquid is the temperature at which a liquid changes to a gas throughout the liquid.

Note that when evaporation takes place, no bubbles are formed in the liquid. However, when boiling takes place, bubbles are formed throughout the liquid.

When a gas is cooled, the particles slow down and a liquid is formed. Condensation is often seen in a kitchen when steam (gas) meets the much colder glass in a window. It may also be seen on a cold day when the warm water vapour that you are breathing out condenses.

Condensation is the changing of a gas to a liquid.

When condensation occurs, the particles lose energy as the gas changes to a liquid.

The various changes of state are summarised in Figure 9.6.

Note from Figure 9.6 that a liquid can be changed into a solid by cooling the liquid, e.g. water freezes to ice. The temperature at which this occurs is called the freezing point.

The **freezing point** is the temperature at which a liquid changes to a solid.

As in the case of condensation, the particles lose energy when a liquid changes to a solid.

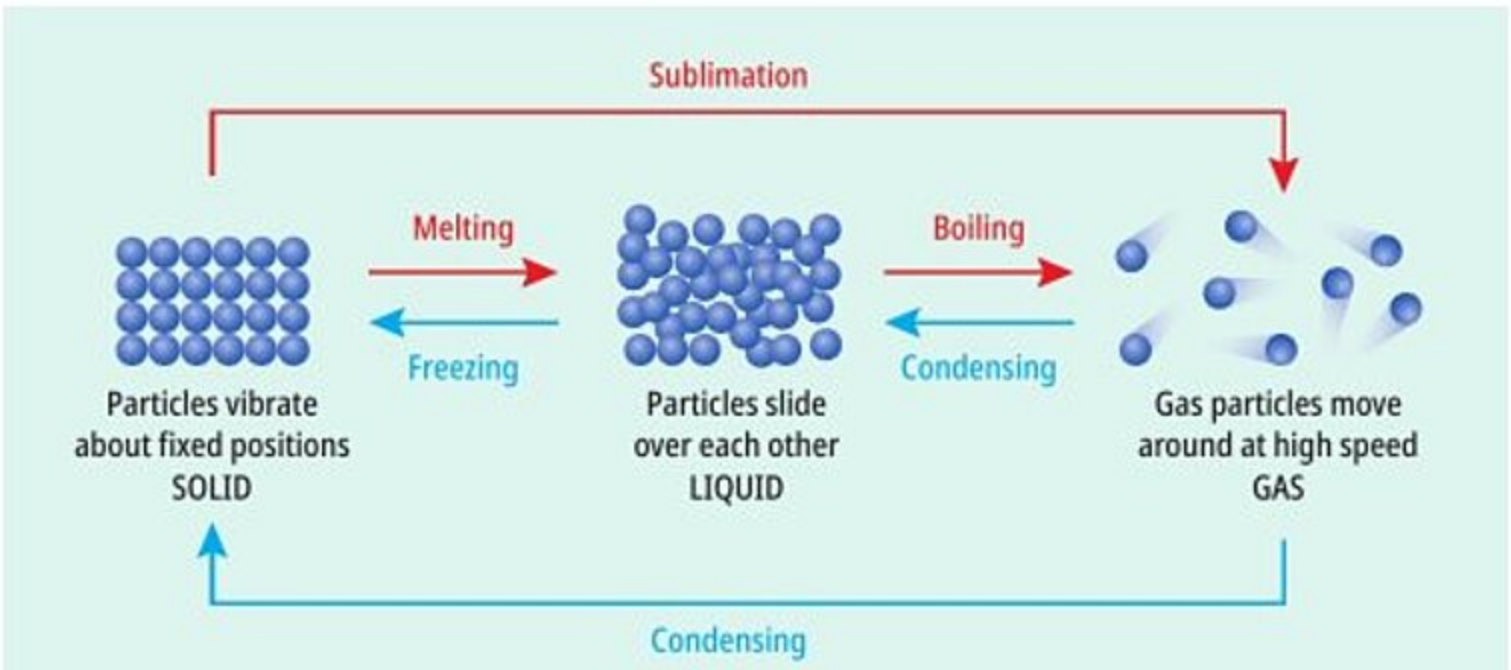


Figure 9.6 The state of a substance can be changed by heating or cooling.

5. Forces between particles

We have already discussed the forces between particles (Chapter 6). We saw that, in solids, the particles are held tightly together by strong forces and this gives solids a definite shape. The forces in liquids are weaker and these weaker forces allow the particles to slide over each other. Therefore, liquids flow. In gases, the forces are very weak and gases can diffuse to fill all the available space.

6. Pressure in gases

The Kinetic Theory of Matter explains how gases exert a pressure. This pressure is caused by the gas particles colliding with each other and with the walls of the container. As the temperature is raised, the particles gain more energy and this additional energy increases the pressure. We will study the relationship between temperature and pressure in more detail later in this chapter.

A **gas** is a substance that has no well-defined boundaries but diffuses rapidly to fill any container in which it is placed.

The ability of a gas to diffuse is often used to define what a gas is.

If you study Figure 2.1 (p.9), you will notice that the white ring is closer to one end (the hydrogen chloride end) of the tube. This shows that the lighter ammonia molecules diffused more quickly than the heavier hydrogen chloride molecules.

9.3 Evidence for the Kinetic Theory of Matter

Two observations provide evidence for the Kinetic Theory of Matter.

1. Brownian motion

This type of motion is named after Robert Brown (Figure 9.7). In his work as a botanist, he spent a lot of time using microscopes to help classify plants. In 1827 he was viewing a suspension of pollen in water under the microscope. To his surprise, he noticed that the individual grains of pollen were moving about in an irregular way. He also observed this type of erratic motion in dye particles. Brown noted his observations but could not explain what was happening. This type of motion was called 'Brownian motion'.

Brown observed the tiny pollen grains moving in a random, zig-zag, irregular fashion because the pollen grains were involved in collisions with the water molecules in the suspension being viewed under the microscope. The kinetic energy possessed by these water molecules causes them to be continuously moving and colliding with the pollen grains. Since the collisions are random, the movement of the pollen grains is also random, irregular and unpredictable. Therefore, Brownian movement provides evidence for the Kinetic Theory of Matter, since this theory proposes that the molecules of water are continuously in motion.

A diagrammatic representation of Brownian motion is shown in Figure 9.8. This observed movement is used to define Brownian motion.

Figure 9.7

Robert Brown
(1773–1858)

Robert Brown was a Scottish botanist who spent some time in Ireland collecting plants. He also spent some time in Australia and returned to Scotland with over four thousand species of plants. In 1827, as he was viewing a suspension of pollen in water under the microscope, he noted that the individual grains were moving about irregularly.

Brownian motion is the random, irregular, zig-zag and continuous movement of tiny particles (such as pollen grains or smoke particles) suspended in a liquid or gas. The movement results from the collisions of these tiny particles with the molecules of the liquid or gas.

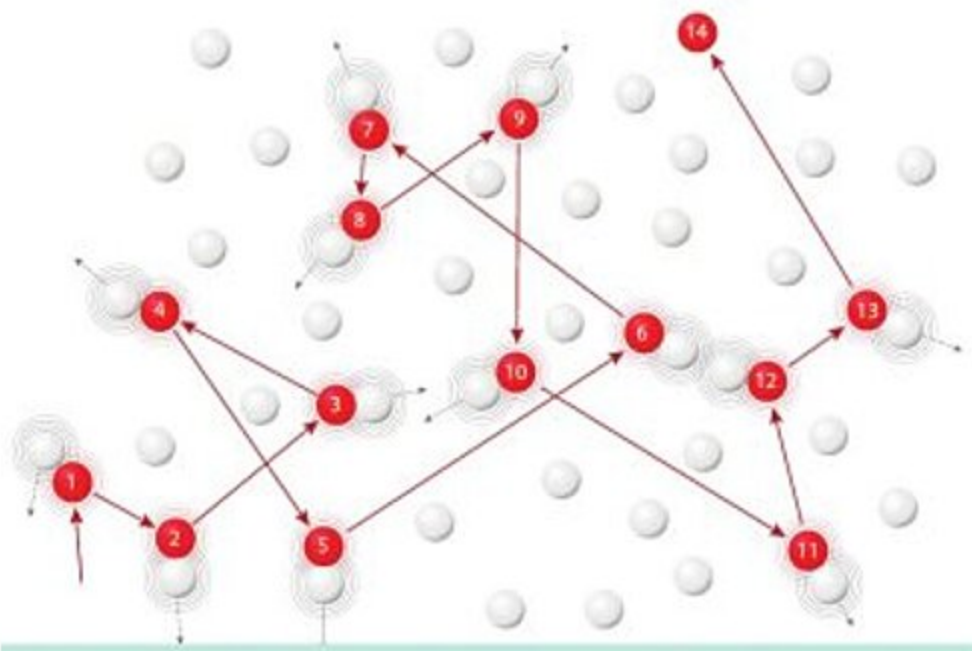


Figure 9.8 This diagram represents Brownian motion observed under the microscope.

Brownian motion provides physical evidence for the Kinetic Theory of Matter. As well as supporting the Kinetic Theory of Matter, it also provides evidence for the existence of atoms and molecules.

9.1 Teacher Demonstration Experiment

Teacher Demonstration Experiment 9.1

Demonstrate Brownian Motion

A video demonstrating this experiment is available online.

Brownian motion may be demonstrated in the laboratory by observing smoke particles trapped in a small 'smoke cell', Figure 9.9

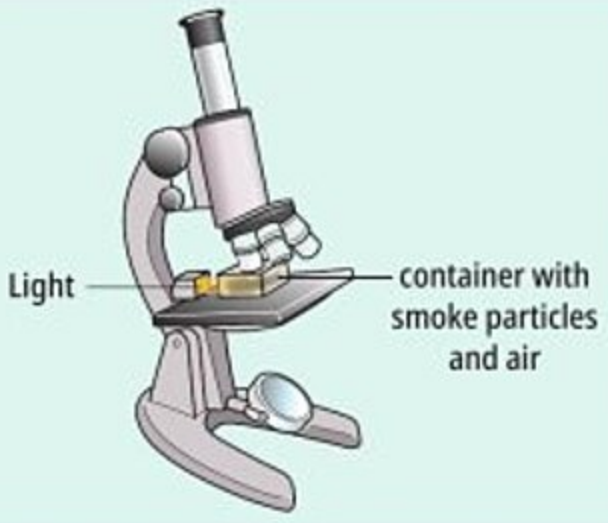


Figure 9.9 Using a microscope, the tiny smoke particles suspended in air may be observed moving about in an irregular way. The smoke particles are continuously colliding with the molecules of the gases in the air.

The **Kinetic Theory of Matter** states that all matter is made up of tiny particles (atoms or molecules) that are in constant random motion. Both **Brownian motion** and **diffusion of gases** provide observable evidence for this theory.

How does Brownian motion provide evidence for the Kinetic Theory of Matter?

The random, zig-gag, irregular movement of the visible particles (pollen or smoke particles) is observed because they are constantly being bombarded by much smaller, invisible molecules of water or gases in the air. Since Brownian motion is continuously taking place, the smaller molecules must be continuously in motion.

2. Diffusion of gases

We have already discussed the concept of diffusion in Chapter 2 and in the introduction to this chapter.

Diffusion is the process by which small particles (atoms, molecules or ions) move from an area of higher concentration to an area of lower concentration.

- Diffusion is a normal process and does not require any external energy to be applied. It occurs due to the natural kinetic energy of the small particles.
- Diffusion can occur in gases, liquids and solids. Diffusion in a liquid may be seen if a large crystal of copper sulfate is placed at the bottom of a large graduated cylinder filled with water. After a few hours, the blue colour will have spread throughout the water. The Cu^{2+} and SO_4^{2-} ions have diffused throughout the water. Diffusion can also occur between two solids that are in contact with each other, but the rate of diffusion is usually much slower than in gases and liquids.

How does diffusion provide evidence for the Kinetic Theory of Matter?

The observable evidence of diffusion demonstrates that particles must be in constant motion, colliding with each other and spreading out to occupy all the available space as stated in the assumptions of the Kinetic Theory of Matter. The only way to explain the results of the experiment shown in Figure 9.10 is in terms of the Kinetic Theory of Matter.

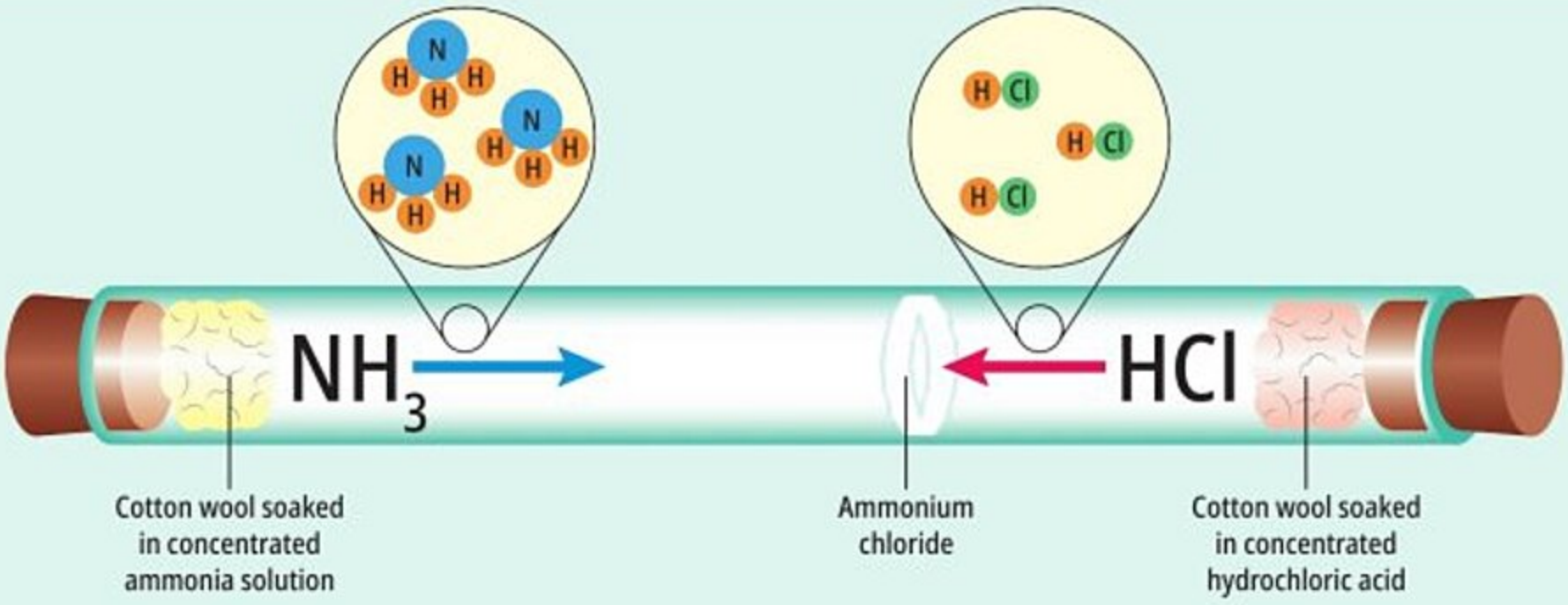


Figure 9.10 The molecules of ammonia gas diffuse from left to right. The molecules of hydrogen chloride gas diffuse from right to left. A white ring of ammonium chloride is formed when the ammonia and hydrogen chloride react with each other. Note that the white ring is closer to one end (the hydrogen chloride end) of the tube. This shows that the lighter ammonia molecules diffused more quickly than the heavier hydrogen chloride molecules.

The equation that describes what happens when the two gases meet to form the solid ammonium chloride may be written as:

$$\underset{\text{ammonia}}{NH_{3(g)}} + \underset{\text{hydrogen chloride}}{HCl_{(g)}} \rightarrow \underset{\text{ammonium chloride}}{NH_4Cl_{(s)}}$$

In short, both Brownian motion and diffusion of gases provide us with strong, observable evidence that tiny particles are in constant, random motion. This evidence is in keeping with the Kinetic Theory of Matter.

TEST YOURSELF: Attempt Questions 9.1 and W9.1–W9.2.

9.4 Relationships between volume, pressure and temperature of gases

We have seen that the particles in a gas have greater freedom of movement than those in a solid or liquid.

Gases also differ from solids and liquids because gases do not have a fixed volume – they expand to fill the container in which they are placed. The volume of the gas is the volume of the container. Since a gas can be either compressed or allowed to expand, the volume of a sample of gas depends on temperature and pressure, Figure 9.11.

Figure 9.11 The volume occupied by the fixed amount of air in the balloon depends on the pressure that the gas in the balloon exerts on the balloon. As the pressure outside the balloon is decreased by pumping air out of the bell jar, the air inside the balloon now occupies a greater volume.

We will study the relationship between volume and pressure in more detail later on in this chapter.

Before studying some of the laws that gases obey, it is important that we understand how to measure the three main properties of a fixed amount of gas: **volume**, **pressure** and **temperature**. Let us first discuss what these terms mean and the units in which they are measured.

Volume

- The volume of a sample of gas is the same as the volume of the container in which the sample is held.
- The SI unit of volume is the cubic metre (m^3). However, this unit is too large for ordinary laboratory work.
- In the laboratory, we normally measure volume in cubic centimetres (cm^3) or **litres** (L). In this textbook we shall use the symbol L to represent litres rather than the small letter l which can easily be confused with the number 1.
- A litre is also called a **cubic decimetre** (dm^3). A cubic decimetre is exactly the same volume as a litre. (A decimetre is one tenth of a metre, i.e. 10 cm. If you make a cube of length 10 cm, the volume of the cube will be 10 cm × 10 cm × 10 cm = 1000 cm^3, i.e. one litre or one cubic decimetre.)

1 cubic metre = 1 metre × 1 metre × 1 metre

= 100 cm × 100 cm × 100 cm

= 10^6 cm^3

(i.e. 1 000 000 cm^3 or 1 million cm^3)

i.e. **1 m^3 = 10^6 cm^3.**

If you were asked to fit sugar lumps of volume 1 cm^3 into a cubic metre, you could fit in a million of them, Figure 9.12. Think about this.

1 litre = 1000 cm^3 = 1 cubic decimetre (dm^3).

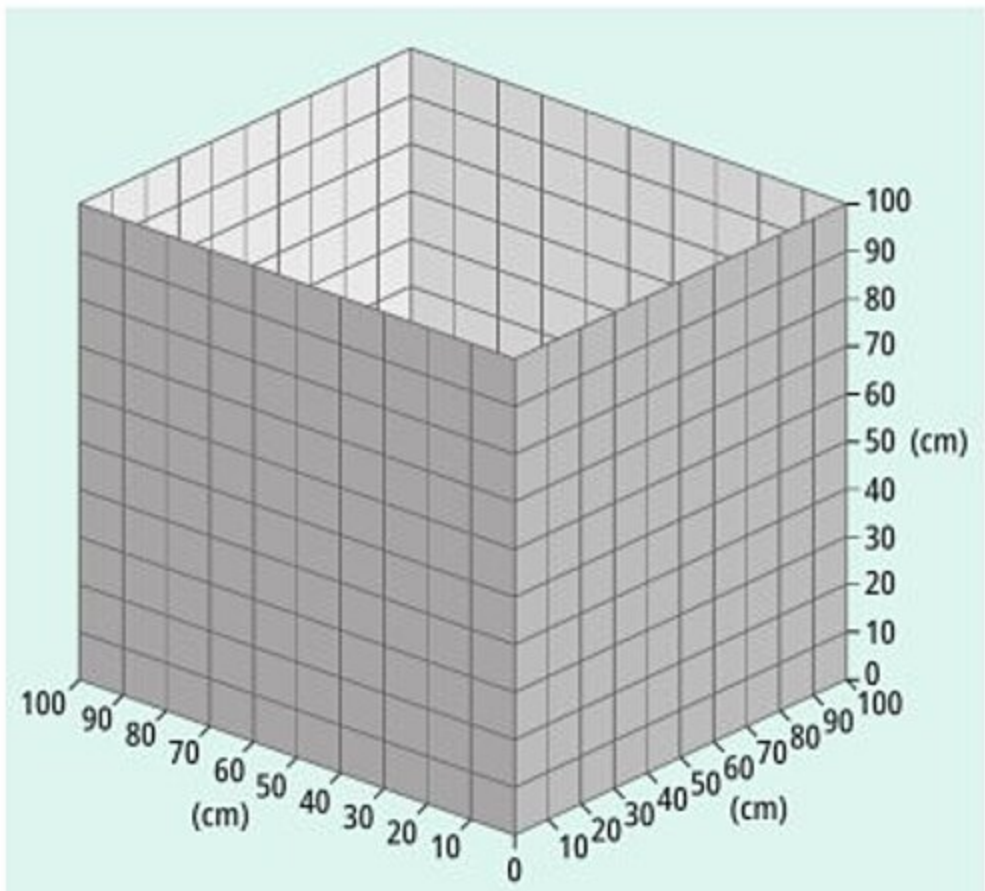


Figure 9.12 A volume of 1 m^3 is equal to 10^6 cm^3.

EXAM TIP!

Remember that 1 m^3 is equal to 1 × 10^6 cm^3 , as you will need this information for calculations in exams.

Temperature

The main points about temperature may be summarised as follows.

- Temperature is a measure of the degree of hotness of an object.
- There are two scales of temperature used in science: the **Celsius scale** (also called the **centigrade scale**) and the **Kelvin scale** (also called the **absolute scale**).
- The Celsius scale is named after Anders Celsius who proposed it in 1742, Figure 9.13. This scale takes the freezing point of water as 0 °C and the boiling point of water as 100 °C. These two points are called the two **fixed points** of the Celsius scale. Since the scale is divided into 100 degrees, it is also called the centigrade ('one hundred steps') scale.
- The Kelvin scale is named after Lord Kelvin who was born William Thomson in Belfast in 1824, Figure 9.14. In 1848 he proposed that the energy of molecules of a gas should reach zero at –273 °C.
- Kelvin proposed that the temperature of –273 °C should be considered the lowest possible temperature (absolute zero).
- He set up a new scale of temperature with the zero mark at absolute zero and each degree rise was the same as a degree rise on the Celsius scale.
- The temperature scale proposed by him is called the **Kelvin scale** and is also called the **absolute scale**.
- In theory, at the zero mark of the Kelvin scale, a gas would occupy zero volume if it could be cooled indefinitely without becoming a liquid or a solid.
- A temperature of absolute zero or zero kelvin is given the symbol 0 K. Note that the unit does **not** have the ° degree symbol.
- The SI unit of temperature is the kelvin (symbol K).

The relationship between the Celsius scale and the Kelvin scale is illustrated in Figure 9.15.

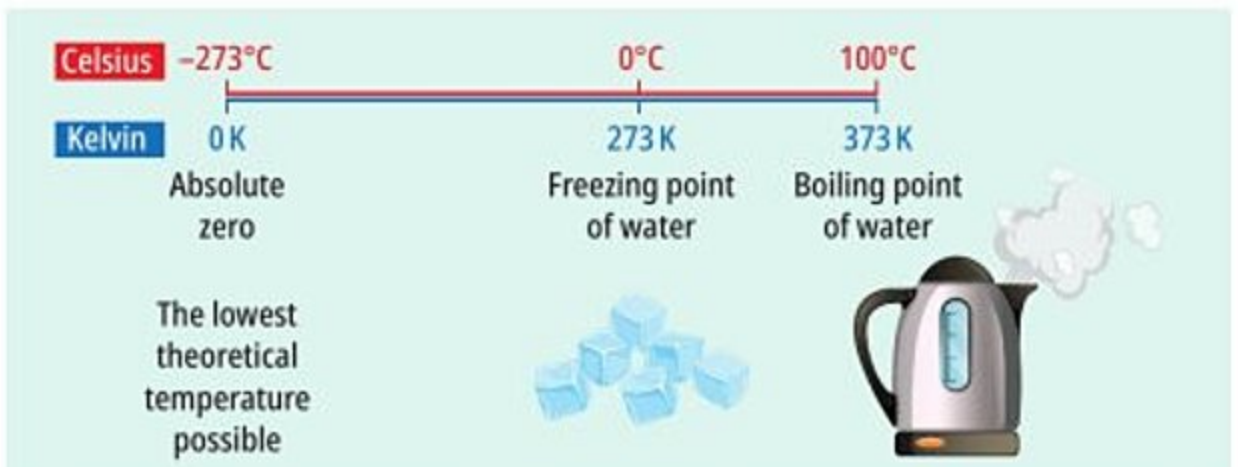


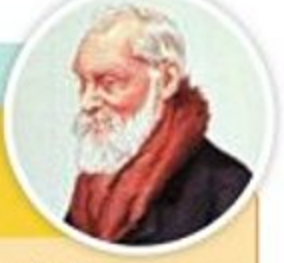
Figure 9.15 The relationship between the Celsius and Kelvin scales of temperature.

Figure 9.13

Anders Celsius
(1701–1744)

Anders Celsius was a Swedish scientist who set up a scale of temperature in which he divided the difference between the freezing point of water and the boiling point of water into 100 degrees.

Figure 9.14



William Thomson
(1824–1907)

William Thomson, also known as Lord Kelvin, was born in Belfast. He was a child prodigy (genius) and attended his father's lectures in mathematics at the age of eight. He proposed a new scale of temperature with its zero mark at absolute zero (–273 °C).

$0\ °C = 0 + 273 = 273\ K$

$50\ °C = 50 + 273 = 323\ K$

$100\ °C = 100 + 273 = 373\ K$

$-273\ °C = -273 + 273 = 0\ K$

Temperature can be converted from the Celsius scale to the Kelvin scale by adding 273 to the Celsius scale.

Note that a difference in temperature is the same for both scales as the size of a degree on the Celsius scale is the same as that on the Kelvin scale. For example, a rise in temperature of 10 °C is the same as a rise in temperature of 10 K. In the SI system, the unit of temperature is the kelvin.

Pressure

- The pressure of a gas is the force that the gas exerts on a unit area (e.g. one square metre) of its container.
- In the SI system, pressure is measured in **newtons per metre squared**, $N\ m^{-2}$. This is also called the **pascal** (Pa).
- Normal atmospheric pressure is approximately $1 \times 10^5\ N\ m^{-2}$ also written as 1×10^5 Pa or 100 000 Pa.
- As the pascal is a small unit of pressure, the **kilopascal**, symbol kPa, is also used (1 kPa = 1000 Pa)
- Weather forecasters often use hectopascals (1 hPa = 100 Pa). Thus, normal atmospheric pressure is 100 kPa (or 1000 hPa). If you find it difficult to remember prefixes such as 'kilo' and 'hecto', their meanings are given in the SEC *Formulae and Tables* booklet.

Normal atmospheric pressure = 1×10^5 Pa = 100 kPa

Standard temperature and pressure (s.t.p.)

The volume of a gas varies with temperature and pressure. Therefore, to compare volumes of gases, the temperature and pressure at which they are measured must be known. Thus, when comparing volumes occupied by gases, it is normal to measure all volumes at the same temperature and pressure. For this reason, chemists decided to measure volumes of gases at **standard temperature and pressure (s.t.p.)**. The standards that have been chosen are:

Standard temperature = 273 K (i.e. 0 °C, the freezing point of water)

Standard pressure = 1×10^5 Pa = 100 kPa

To be more precise, standard pressure is actually 1.01325×10^5 Pa. However, for all calculations in this course, we may use the approximate value of 1×10^5 Pa or 100 kPa. **If you are told on an exam paper to use the value of standard pressure in the SEC *Formulae and Tables* booklet, then use 1.01325×10^5 Pa**.

If you study a wide variety of gases, you will find that they differ from each other in many ways, e.g. some are flammable, some are coloured, some are vital to maintain life and others are poisonous. However, scientists have found that even though gases have different physical and chemical properties, all gases obey certain laws.

We now consider the five main laws that determine the behaviour of gases.

1. Boyle's Law

In 1662 the Irish chemist Robert Boyle (also referred to in Chapter 4, as he was the first person to give an accurate definition of an element) built an air pump in order to study the properties of gases, Figure 9.16. He used this pump to investigate how the volume of a fixed mass of gas, kept at constant temperature, varied with changes in pressure.

Figure 9.16 Robert Boyle built this air pump to study the relationship between the volume and pressure of a gas.

Imagine a sample of gas trapped in a container with a movable piston, similar to what you have in a bicycle pump, Figure 9.17.

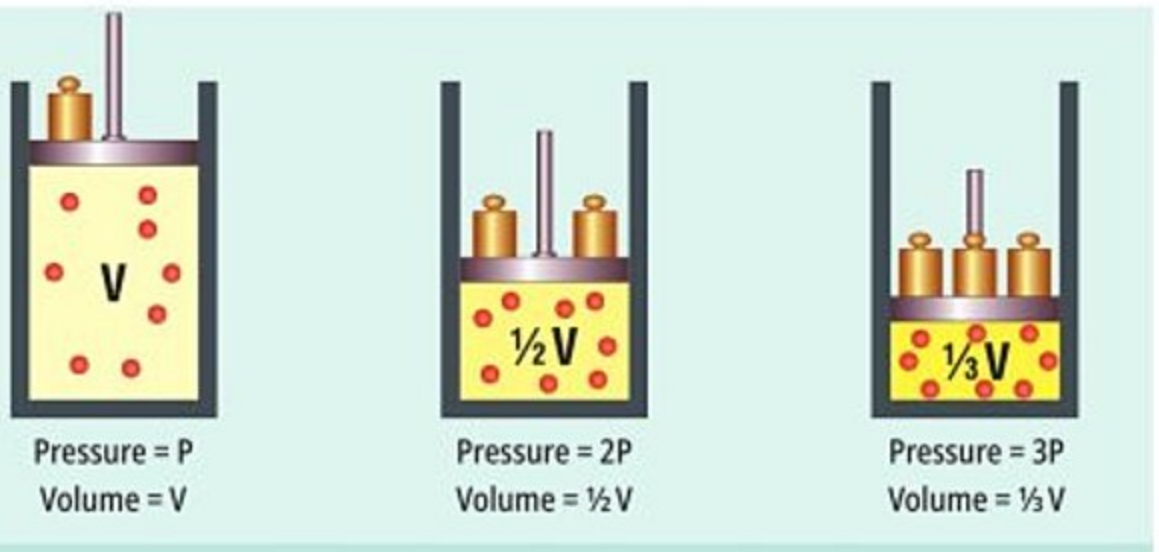


Figure 9.17 As the pressure is increased, the volume is decreased.

Boyle found that as the pressure of a gas increased, the volume decreased. In other words, volume is inversely proportional to the pressure, Figure 9.18(a). To check that this was correct, Boyle plotted the values of pressure against the inverse of volume as shown in Figure 9.18(b). The straight-line graph passing through the origin that he obtained showed that the pressure and volume of the gas were inversely proportional.

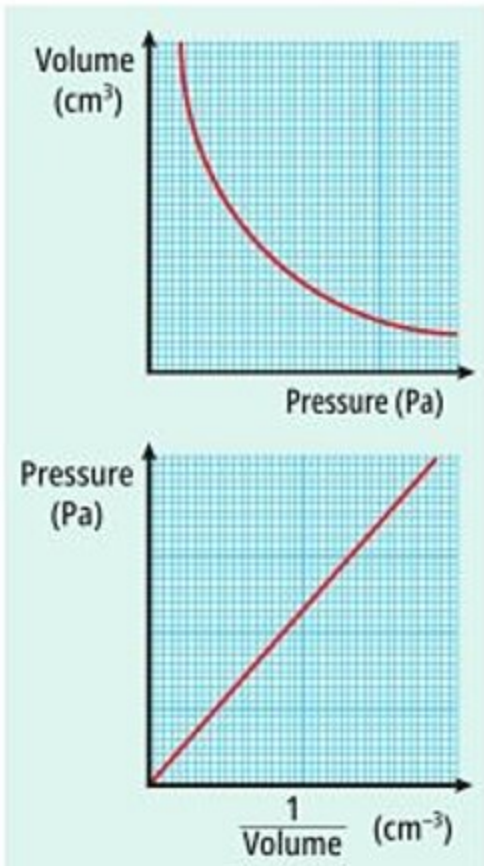


Figure 9.18 (a) As the pressure increases, the volume decreases. (b) Pressure is inversely proportional to volume.

Boyle found that this relationship was true for all the gases he studied, regardless of their different properties. In 1662 he summarised his results in a statement that is now known as Boyle's Law.

A modern method of verifying Boyle's Law is shown in Figure 9.19.

Figure 9.19 A modern method of verifying Boyle's Law. The pressure is increased on the air in the plastic syringe.

Boyle's Law states that, at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.

This pressure is measured by means of a pressure sensor and the data are recorded on the computer. For each pressure value, the corresponding value of the volume of the gas is read off.

The computer plots a graph of Pressure vs $\frac{1}{\text{Volume}}$.

How do we explain Boyle's Law?

Boyle's Law may be explained using the Kinetic Theory of Matter.

- A gas is made up of particles (atoms or molecules) which are continuously in motion. If you look back at Figure 9.17, if you push down on the plunger, the volume of the container is decreased.
- Therefore, the molecules are now moving within a smaller space.
- Therefore, they collide more frequently with each other and with the walls of the container.
- The increased number of collisions causes an increase in the pressure.

The reverse of the above happens if you pull the plunger up. The molecules of the gas have more space to spread out. Therefore, the molecules collide less often with each other and with the walls of the container. Therefore, the pressure decreases.

Boyle's Law can be expressed mathematically as:

$$V \propto \frac{1}{p}$$

The symbol ∝ stands for 'is proportional to'.

Therefore, $V = k\frac{1}{p}$ where k is a constant of proportionality.

This is another way of proving Boyle's Law, i.e. you only need to show that the pressure of a fixed mass of the gas multiplied by its volume is always a constant value. This is shown in Table 9.2.

Pressure (p) (kPa)	Volume (V) (L)	Pressure × volume $p \times V$
40	0.100	4.0
67	0.060	4.0
80	0.050	4.0
100	0.040	4.0
120	0.033	4.0
160	0.025	4.0

Table 9.2 Data obtained from compressing a sample of air at 25 °C.

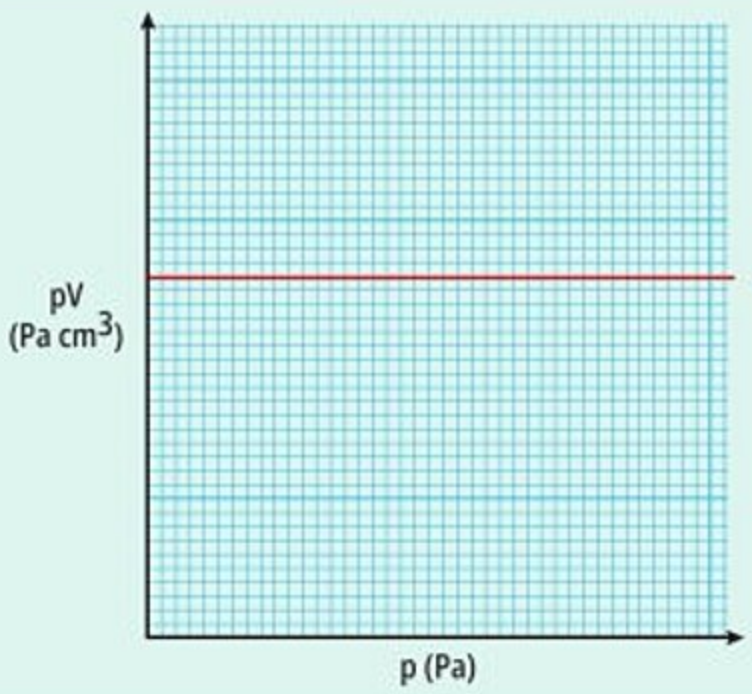


Figure 9.20 A plot of pV against p is a straight line.

Therefore, since pV is always a constant value, if pV is plotted against p, a graph similar to that shown in Figure 9.20 will result, i.e. at different values of p, the value of pV will always be the same.

2. Charles' Law

We have seen that Robert Boyle studied the relationship between the volume and pressure of a fixed mass of gas at constant temperature. A French scientist, Jacques Charles, also studied gases and, in 1783, he constructed the first hydrogen balloon, Figure 9.21. He noticed that, as the balloon went higher, the temperature decreased and the volume of the gas in the balloon also decreased.

Figure 9.21 This drawing shows Jacques Charles and his colleague Marie-Noël Robert in the first hydrogen balloon flight in 1783. They ascended to an approximate height of 1.6 km over Paris.

On returning to his laboratory, he investigated the relationship between the volume and temperature of a fixed mass of gas at constant pressure. He carried out an experiment similar to that shown in Figure 9.23. Imagine a fixed mass of gas trapped by a thin thread of concentrated sulfuric acid in a long glass tube as shown in Figure 9.22. The tube is sealed at the bottom and open at the top. As the water is heated, the volume of trapped air increases and the concentrated sulfuric acid is pushed up the tube.

Charles summarised the results of his experiments on a graph similar to that shown in Figure 9.23.

You will observe that the straight line in Figure 9.23 does not pass through the origin. Therefore, one cannot say that the volume of the gas is directly proportional to the temperature measured in °C. However, if the line is continued backwards, it cuts the X axis at –273 °C, Figure 9.24.

As already stated, this temperature of –273 °C is taken as the starting point for the Kelvin or absolute scale of temperature. As shown in Figure 9.24, using this scale of temperature there is now a direct relationship between volume and temperature. This relationship is stated in Charles' Law:

Charles' Law states that, at constant pressure, the volume of a fixed mass of gas is directly proportional to its temperature measured on the Kelvin scale.

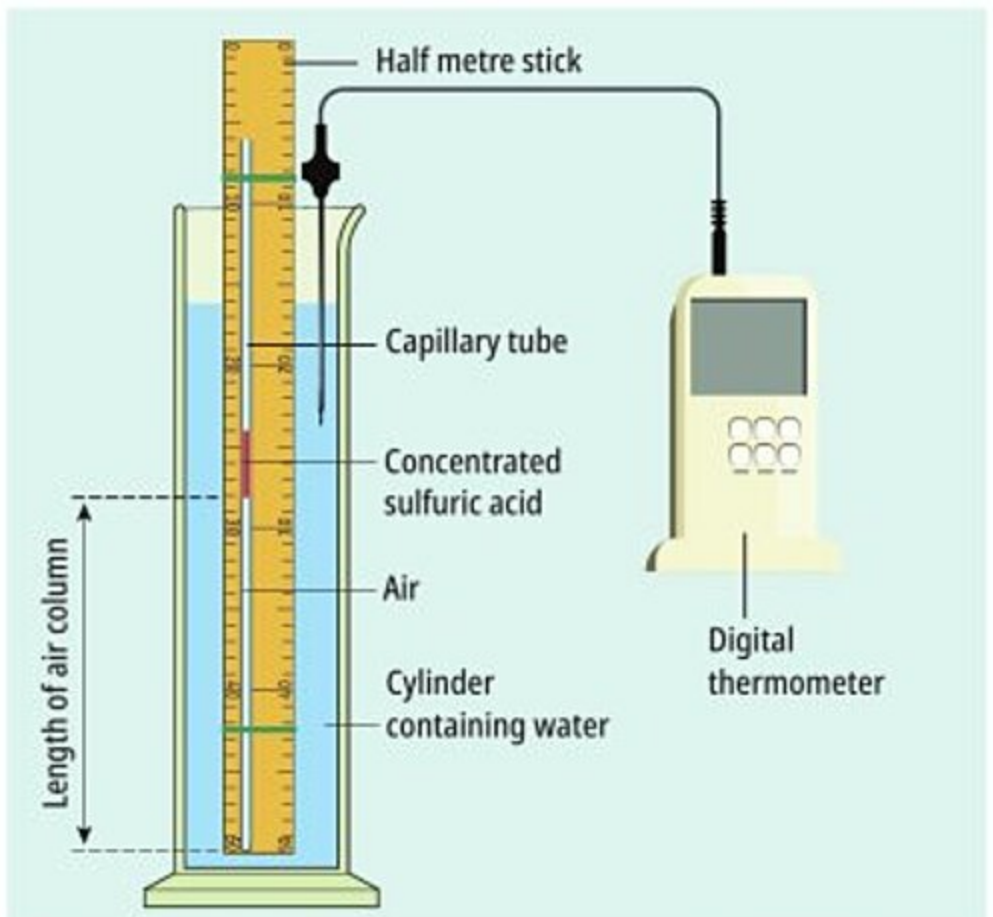


Figure 9.22 Apparatus to investigate Charles' Law. As the temperature of the trapped air increases, its volume also increases and this pushes the concentrated sulfuric acid upwards.

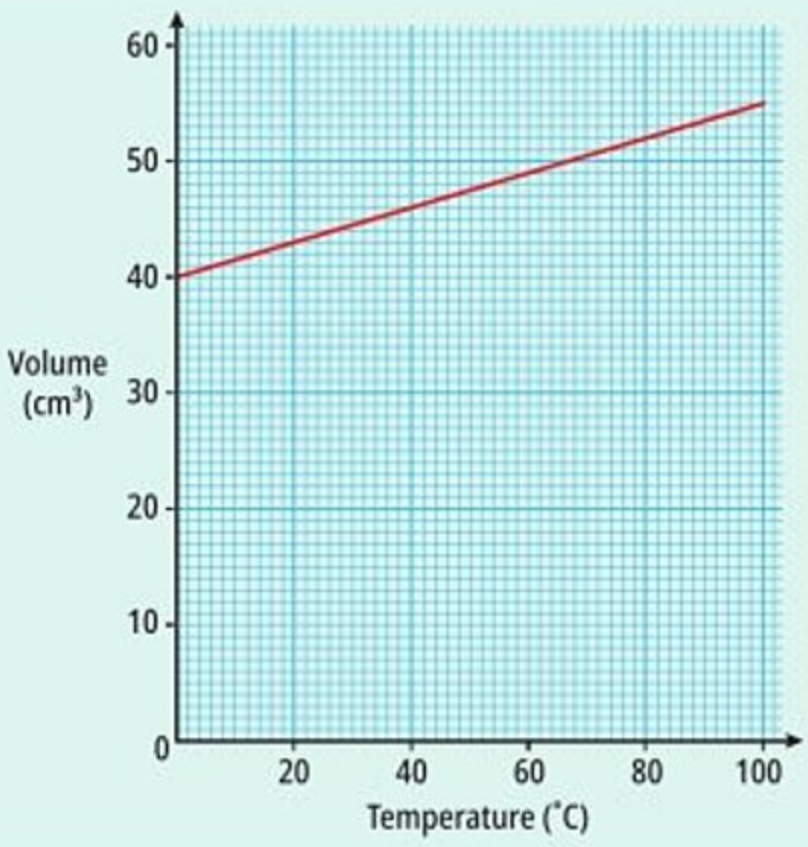


Figure 9.23 The volume of the gas increases as the temperature is increased.

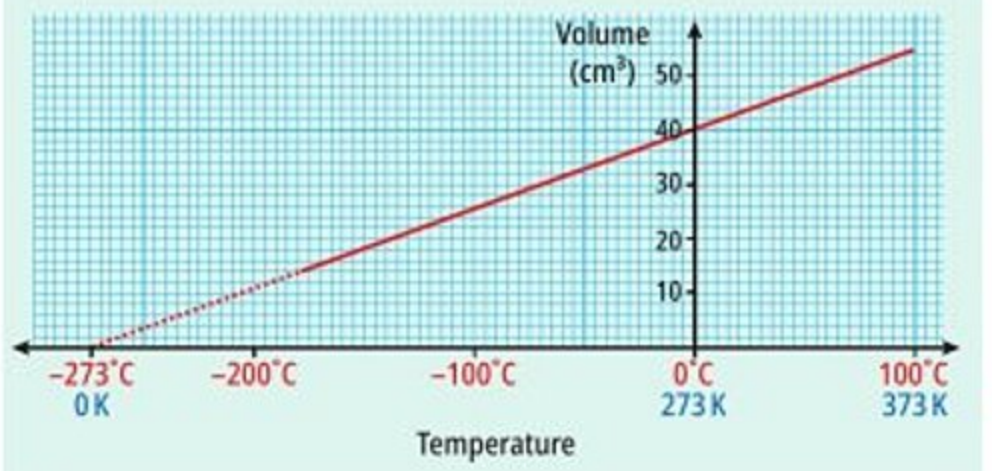


Figure 9.24 Volume is directly proportional to temperature on the Kelvin scale.

How do we explain Charles' Law?

Charles' Law may be explained using the Kinetic Theory of Matter. A gas is made up of particles (atoms or molecules) which are continuously in motion. Consider Figure 9.25.

- If the temperature of the container is increased, the molecules are now moving more quickly due to the extra kinetic energy they obtain from the heat supplied.
- This means that the molecules collide more frequently and more forcefully with each other and with the walls of the container.
- In order to prevent an increase in pressure, it is necessary to give the molecules more room in which to move around.
- Therefore, the volume of the container increases.

The reverse happens if you cool the gas. Cooling the gas slows down the molecules, as they now have less kinetic energy. Therefore, they collide with each other and with the walls of the container less often and less forcefully. In order to prevent a decrease in pressure, it is necessary to give the molecules less room in which to move around. Therefore, the volume of the container decreases.

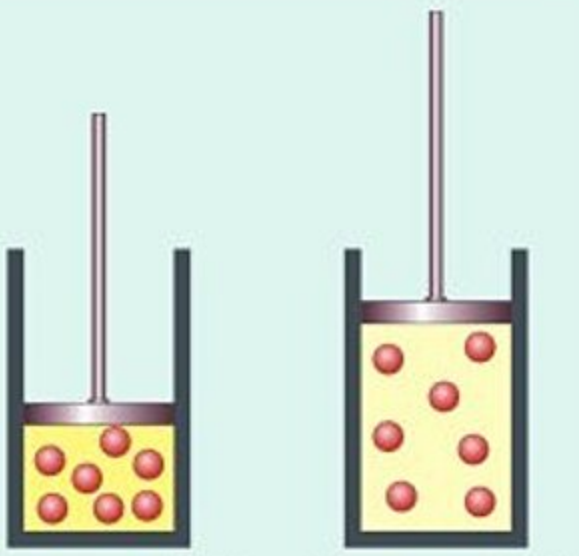


Figure 9.25 In order to keep the pressure constant as the container is heated, the volume of the container must increase.

Mathematically, Charles' Law may be stated as:

$V \propto T$ provided T is measured on the Kelvin scale.

$V = k\,T$ where k is a constant of proportionality.

$$\frac{V}{T} = k$$

This is another way of proving Charles' Law, i.e. dividing the volume of the gas by its temperature (measured on the Kelvin scale) always gives a constant value. This is shown in Table 9.3.

Volume (cm³)	T (°C)	T (K)	$\frac{V}{T}$
75	–173	100	0.75
150	–73	200	0.75
225	27	300	0.75
300	127	400	0.75
375	227	500	0.75

Table 9.3 Data obtained by heating a sample of hydrogen at atmospheric pressure.

Therefore, since $\frac{V}{T}$ is always a constant value, if $\frac{V}{T}$ is plotted against T, a straight-line graph as shown in Figure 9.26 should result, i.e. at different values of T, $\frac{V}{T}$ always has the same value.

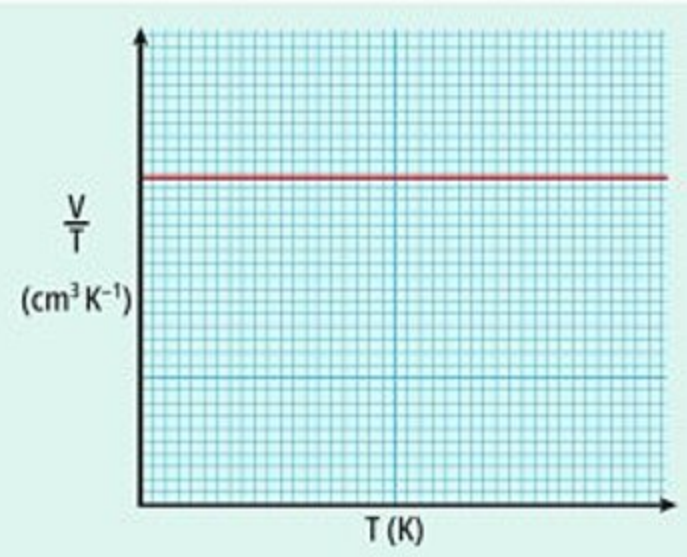


Figure 9.26 A plot of $\frac{V}{T}$ against T is a straight line.

3. The Combined Gas Law

We have seen from Boyle's Law that $pV = k$.

Therefore, if the volume of a gas is allowed to change from V_1 to V_2 and its pressure changes from an initial value of p_1 to a final value of p_2 (keeping the temperature constant), then we can say:

$$p_1V_1 = p_2V_2$$

(This may also be seen from Table 9.2: Any particular value of pressure multiplied by its corresponding volume is equal to any other value of pressure multiplied by its corresponding volume.)

Similarly, from Charles' Law: $\frac{V_1}{T_1} = \frac{V_2}{T_2}$

Combining Boyle's Law and Charles' Law, the following equation is obtained:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

This is called the **Combined Gas Law.** (It is also called the General Gas Law but, since the term *Combined Gas Law* is used more widely, we will use it in this textbook.) Always remember that pressure, volume, and temperature of gases are always linked. **The Combined Gas Law** is very useful for converting between these three variables under one set of conditions (p_1, V_1, T_1) to what they would be under a different set of conditions (p_2, V_2, T_2). This type of calculation is illustrated in Example 9.1.

Example 9.1

Question

A sample of nitrogen gas has a volume of 75 cm^3 at a temperature of 27 °C and a pressure of 95 kPa. Find the volume that the gas would have at s.t.p.

Answer

Summarise the data given as shown in Table 9.4.

Given	s.t.p.
$V_1 = 75\ cm^3$	$V_2 = ?$
$p_1 = 95$ kPa	$p_2 = 100$ kPa
$T_1 = 27\ °C + 273 = 300$ K	$T_2 = 0\ °C + 273 = 273$ K

Table 9.4

Substitute into:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

$$\frac{95 \times 75}{300} = \frac{100 \times V_2}{273}$$

$$V_2 = \frac{95 \times 75 \times 273}{300 \times 100}$$

$$= 64.84\ cm^3$$

Answer: 64.84 cm^3

EXAM TIP!

Since the Combined Gas Law is derived from Charles' Law, do not forget to **convert all temperatures to the Kelvin scale**. Remember that Charles' Law is only true when temperature is measured on the Kelvin scale.

EXAM TIP!

The units on either side of the equation must be consistent. The question gives pressure in kilopascals. These units are used for pressure on the left-hand side of the equation. Therefore, standard pressure must be written in kilopascals on the right-hand side of the equation. This also applies to the units for volume. In the question, the volume is given in cm^3. Therefore, the volume in the answer will also be in cm^3.

TEST YOURSELF: Attempt Questions 9.2–9.5 and W9.3–W9.5.

4. Gay-Lussac's Law of combining volumes

Joseph Gay-Lussac (Figure 9.27) was a French chemist who was interested in what happens when gases react with each other. In 1805 he was studying the reaction between hydrogen and oxygen.

He confirmed that when hydrogen reacts with oxygen, two volumes of hydrogen always react with one volume of oxygen to form two volumes of steam (all volumes being measured under the same conditions of temperature and pressure).

i.e. hydrogen	+	oxygen	→	steam
2 volume		**1 volume**		**2 volumes**

Note the simple ratio 2:1:2.

This led him to study the reactions of other gases to see whether they reacted in simple ratios also. Some of the reactions which he studied were:

hydrogen	+	chlorine	→	hydrogen chloride	
1 volume		**1 volume**		**2 volumes**	**(simple ratio 1:1:2)**
nitrogen monoxide	+	oxygen	→	nitrogen dioxide	
2 volumes		**1 volume**		**2 volumes**	**(simple ratio: 2:1:2)**

In 1808 Gay-Lussac summarised the results of his work in his Law of Combining Volumes.

Figure 9.27 Joseph Gay-Lussac (on the left) and his colleague Jean-Baptiste Biot were French scientists who were interested in gases. The drawing shows a balloon flight that they made in 1804 to study the composition of air at high altitudes.

Gay-Lussac's Law of Combining Volumes states that, in a reaction between gases, the volumes of the reacting gases and the volumes of any gaseous products are in the ratio of small whole numbers, provided the volumes are measured at the same temperature and pressure.

Gay-Lussac's law is very helpful as it allows you to predict how much gas you need or how much gas will be produced in a reaction involving gases when all volumes are measured at the same temperature and pressure.

Special types of syringes made of glass called gas syringes are used to study the volumes of gases that react with each other, Figure 9.28.

The results of experiment to study the volume of nitrogen monoxide that reacts with oxygen may be summarised as follows:

- The results of the experiment are plotted on a graph as shown in Figure 9.29.

Tell us that the reaction is complete when approximately 25 cm^3 of oxygen has been added to the 50 cm^3 of nitrogen monoxide, proving that one volume of oxygen reacts with two volumes of nitrogen monoxide.

$2NO$	+	O_2	→	$2NO_2$
nitrogen monoxide	+	oxygen	→	nitrogen dioxide
2 volumes (50 cm^3) (simple ratio 2:1:2)		**1 volumes (25 cm^3)**		**2 volumes (50 cm^3)**

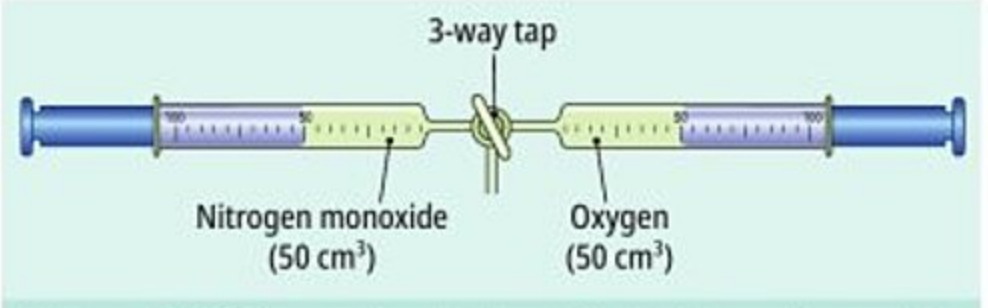


Figure 9.28 Apparatus to investigate the volume of nitrogen monoxide that reacts with oxygen

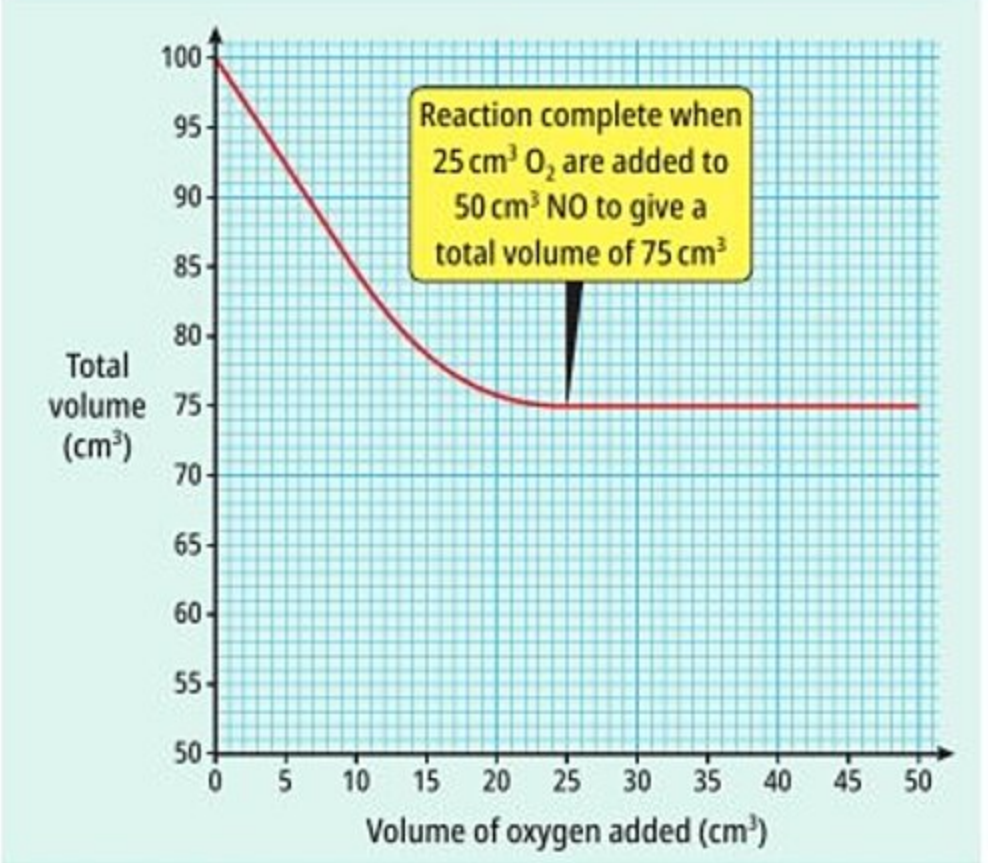


Figure 9.29 The reaction is complete when 25 cm^3 of oxygen is added to 50 cm^3 of nitrogen monoxide to give 50 cm^3 of nitrogen dioxide. The total volume at the end of the experiment is 75 cm^3, since a volume of 25 cm^3 of the original 50 cm^3 of oxygen has not reacted.

This is exactly the type of result that Gay-Lussac obtained in a large number of experiments involving gases, i.e. the volumes of the gases that reacted and the volumes of the gaseous products formed were all in simple whole number ratios to each other.

5. Avogadro's Law

After Gay-Lussac's discovery of the small whole number ratios in which gases react, scientists tried to develop a theory to explain the results of Gay-Lussac's experiments. It seemed likely that the explanation would rely on the idea that gases consist of particles. If this were the case, it would be the number of particles that would be important.

Gay-Lussac's results were published the same year as Dalton's Atomic Theory (1808). However, attempts to explain Gay-Lussac's Law using Dalton's atomic theory failed. Dalton imagined hydrogen and oxygen gas as being made up of **atoms** of hydrogen and oxygen. He could not explain why two volumes of hydrogen should combine with one volume of oxygen.

"Volumi eguali di gas nelle stesse condizioni di temperatura e di pressione contengono lo stesso numero di molecole"
1856
1956
AMEDEO AVOGADRO
POSTE ITALIANE L.25

Figure 9.30 Amedeo Avogadro provided an explanation for Gay-Lussac's Law of Combining Volumes.

He suggested that Gay-Lussac was mistaken and that his observations were inaccurate. It was three years later when Amedeo Avogadro came up with the answer to the problem, Figure 9.30.

Avogadro reasoned as follows: by experiment, it is found that 100 cm^3 of hydrogen reacts exactly with 100 cm^3 of chlorine. This must mean that there is the **same number of molecules** of hydrogen and chlorine in each volume. Otherwise, some molecules of hydrogen or chlorine would be left over.

	hydrogen	+	chlorine	→	hydrogen chloride	
	1 volume		**1 volume**		**2 volumes**	

Suppose 1 volume of hydrogen and 1 volume of chlorine each contains n molecules.

i.e.	n molecules	+	n molecules	→	2n molecules	
	hydrogen		**chlorine**		**hydrogen chloride**	
i.e.	1 molecule	+	1 molecule	→	2 molecules	
	hydrogen		**chlorine**		**hydrogen chloride**	
i.e.	H_2	+	Cl_2	→	2HCl	

Similarly, the other reactions described above when discussing Gay Lussac's Law may be written as:

$2H_2 + O_2 \rightarrow 2H_2O$ $\quad$ $2NO + O_2 \rightarrow 2NO_2$

In other words, the ratio in which the volumes of the gases combine is the same as the ratio in which the molecules of the gases combine. Therefore, when dealing with gaseous reactions, the words 'volume' and 'molecule' can always be interchanged or swapped for each other. The reaction between hydrogen and chlorine is illustrated in Figure 9.31.

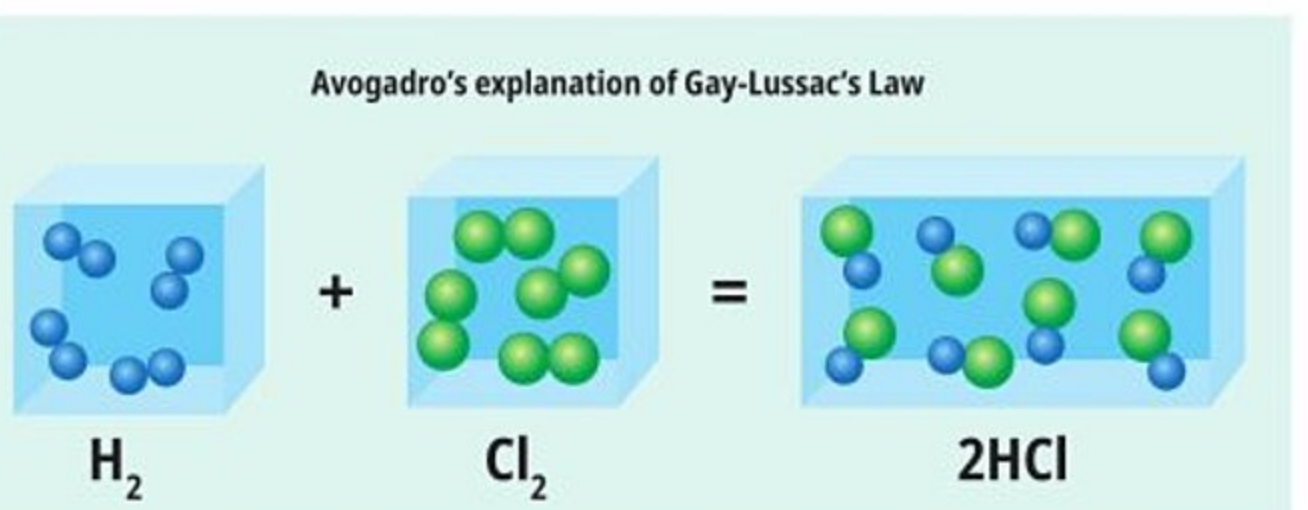


Figure 9.31 Avogadro assumed that equal volumes of gases at the same temperature and pressure contained equal numbers of molecules.

This assumption that Avogadro made is now called **Avogadro's Law** (also called **Avogadro's Theory** or **Avogadro's Hypothesis**) and is stated as follows:

> **Avogadro's Law** states that equal volumes of gases contain equal numbers of molecules under the same conditions of temperature and pressure.

This law is illustrated in Figure 9.32.

Avogadro's Law is an important law in chemistry, as it explains the relationship between the volume of a gas and the number of molecules present. Avogadro's Law was not accepted for nearly 50 years after he proposed it. This was because Dalton's Theory did not allow for the existence of molecules. Avogadro was the first to distinguish between atoms and molecules and introduced the word 'molecule' into the language of chemistry. Using his theory, he also proposed that the water molecule contained two hydrogen atoms for each oxygen atom. His explanation of Gay-Lussac's results for the reaction of oxygen and hydrogen is summarised in Figure 9.33.

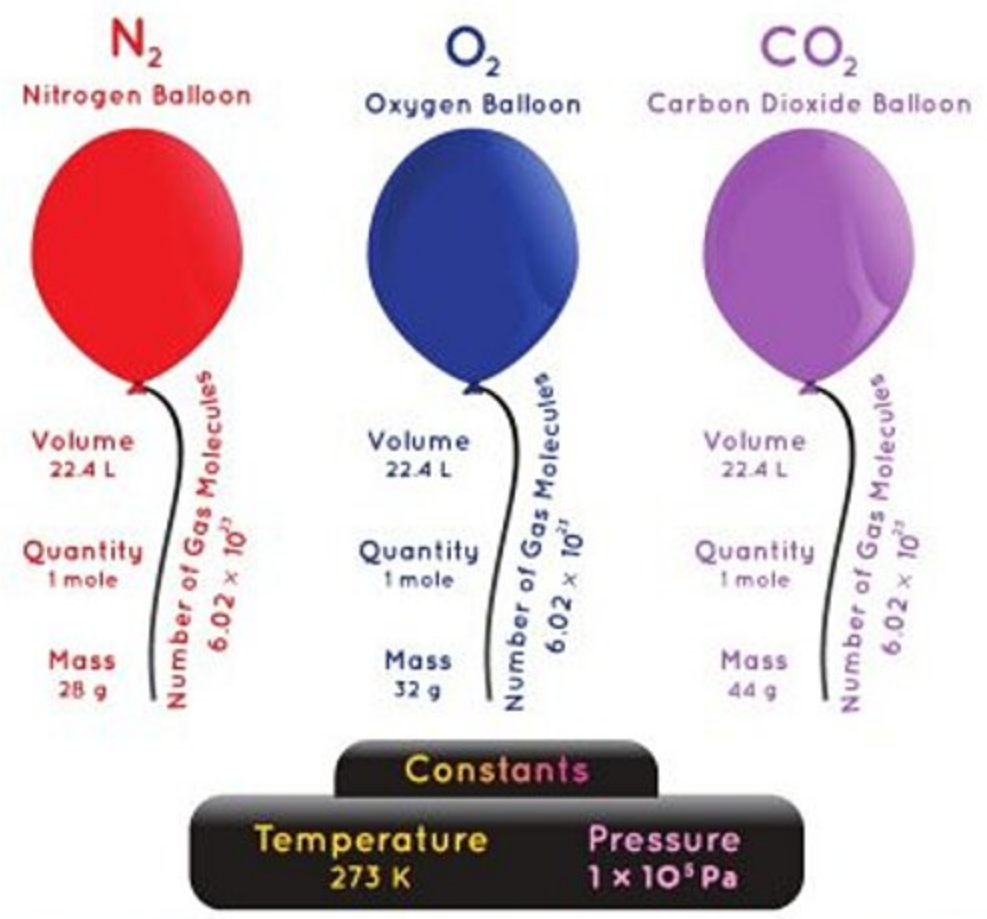


Figure 9.32 Equal volumes of gases contain equal numbers of molecules under the same conditions of temperature and pressure. In the case of one mole of the gas, the volume occupied is 22.4 L at standard temperature and pressure.

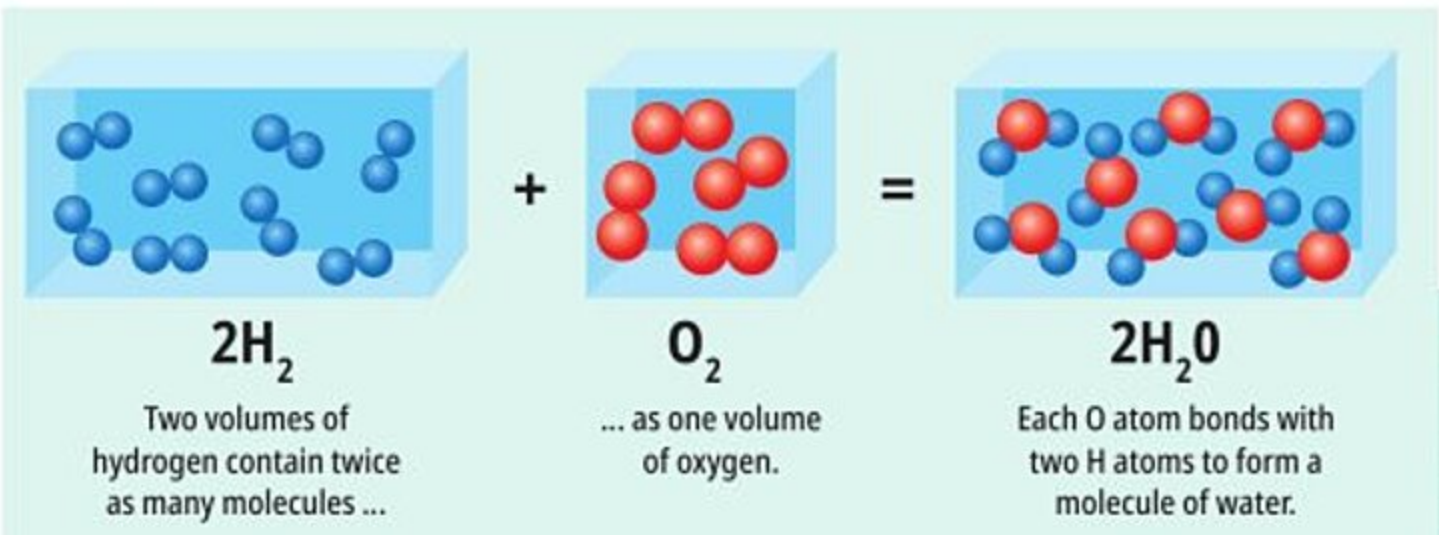

+
=
$2H_2$
Two volumes of hydrogen contain twice as many molecules ...
O_2
... as one volume of oxygen.
$2H_20$
Each O atom bonds with two H atoms to form a molecule of water.

Figure 9.33 Avogadro's Law explains why two volumes of hydrogen react with one volume of oxygen to produce two volumes of steam.

By experiment it is found that a mole of oxygen gas (i.e. 32 g O_2) occupies a volume of 22.4 litres at s.t.p. Since one mole of any gas contains 6.02×10^{23} molecules, then by Avogadro's Law, one mole of any gas should occupy 22.4 litres at s.t.p.

> At s.t.p. one mole of any gas occupies a volume of 22.4 litres.

Note the following:

- The volume occupied by one mole of any gas is called its **molar volume**. Thus, the **molar volume of all gases at s.t.p. is 22.4 litres**. This value is given in the SEC *Formula and Tables* booklet.
- For some calculations, you need to use the molar volume at room temperature and pressure. The value of this quantity is 24.0 litres. Thus, **the molar volume at room temperature and pressure is 24.0 litres**. This value will be given to you if it is required for calculations.

EXAM TIP!

Make sure that you read the exam question carefully to decide if you must use the molar volume at s.t.p. (22.4 litres) or the molar volume at room temperature and pressure (24.0 litres).

How is Avogadro's Law explained by the Kinetic Theory of Matter?

- In a container, equal numbers of gas particles (atoms or molecules) exert equal pressure under the same conditions of temperature and volume.
- Pressure and volume depend on the number of collisions.
- If two gases are at the same temperature, their molecules will have the same average kinetic energy, regardless of the type of molecule.
- The number of collisions is independent of the type of gas.
- It is the number of molecules that determines the pressure and volume not the type of molecules.
- Therefore, under the same conditions of temperature and pressure, equal volumes of gases must contain equal numbers of molecules.

Since one mole of any gas occupies 22.4 L at s.t.p, the density of a gas is easily calculated. This is illustrated in Example 9.2.

Example 9.2

Question

Calculate the density of carbon dioxide at s.t.p.

Answer

Relative molecular mass

$CO_2 = 12.01 + 2(16) = 44.01$

i.e. 1 mole $CO_2 = 44.01$ g

i.e. 44.01 g CO_2 occupy 22.4 L at s.t.p.

$$\text{Density} = \frac{\text{Mass}}{\text{Volume}}$$

$$= \frac{44.01 \text{ g}}{22.4 \text{ L}}$$

$$= 1.96 \text{ g/L}$$

Answer: 1.96 g/L

Example 9.3

Question

Calculate the volume occupied by 20 g of sulfur dioxide gas at s.t.p.

Answer

Relative molecular mass of $SO_2 = 32.07 + 2(16)$
$= 64.07$

1 mole of sulfur dioxide occupies 22.4 L at s.t.p.

i.e. 64.07 g SO_2 occupy 22.4 L

1 g SO_2 occupies $\frac{22.4}{64.07}$ L

Therefore, 20 g SO_2 occupy $= \frac{20 \times 22.4}{64.07}$ L

$= 6.99$ L

Answer: 6.99 L

Example 9.4

Question

200 cm^3 of a certain gas at s.t.p. have a mass of 0.25 g. Calculate the relative molecular mass of the gas.

Answer

200 cm^3 have a mass of 0.25 g

1 cm^3 has a mass of $\frac{0.25}{200}$ g

22 400 cm^3 have a mass of $\frac{22\,400 \times 0.25}{200}$ g = 28 g

i.e. 22.4 L of the gas have a mass of 28 g

Therefore, relative molecular mass of gas = 28

Answer: 28

TEST YOURSELF: Attempt Questions 9.6–9.8 and W9.6–W9.8.

9.5 The Kinetic Theory of Matter applied to gases

We now take a closer look at the Kinetic Theory of Matter as it applies to gases. In order to help us understand the behaviour of gases, a number of assumptions were developed.

Assumptions of the Kinetic Theory of Matter as applied to gases

1. Gases are made up of particles (molecules or atoms) that are in continuous rapid, random motion, colliding with each other and with the walls of the container.
2. There are no attractive or repulsive forces between the molecules of a gas, i.e. the molecules are independent of each other.
3. The gas molecules are so small and so widely separated that the actual volume of all the molecules is negligible compared with the space they occupy. This can be used to explain why equal volumes of gases contain equal numbers of particles when measured under the same conditions of temperature and pressure.
4. When molecules collide, the collisions are perfectly **elastic**, i.e. there is no loss of kinetic energy in these collisions, although there may be a transfer of energy between the colliding particles, Figure 9.34. This means that, if one molecule loses energy in a collision, its partner in the collision gains this energy. (If they stuck together after the collision, the collision would be called an inelastic collision.) You can study some interactive elastic collisions on the PhET University of Colorado website.
5. The average kinetic energy of the molecules in a sample of gas is proportional to the temperature measured on the Kelvin (absolute) scale.

Limitations to the Kinetic theory of Matter as applied to gases

If we examine these assumptions, we see that there are certain limitations to the kinetic theory of gases:

- Contrary to Assumption 2, all real gases actually do have tiny attractive or repulsive forces between the molecules of the gas. As discussed in Chapter 6, gas molecules that are **polar** (e.g. NH_3 and HCl) will have attractive intermolecular forces because the partially negative end of one molecule will be attracted to the partially positive end of another molecule. For example, in the case of NH_3, these intermolecular forces are hydrogen bonds. In the case of HCl, the intermolecular forces are dipole–dipole forces. Similarly, there are weak London dispersion forces between non-polar molecules (e.g. Cl_2, O_2).
- Contrary to Assumption 3, it is not valid to say that the volume of the molecules of a gas is always negligible compared with the space that they occupy. Under very high pressure, when molecules are crowded closer together, it is clear that their volume is not negligible compared with the distances between them.

Therefore, it is true to say that all of the assumptions of the kinetic theory do not hold for real gases but only hold for what is called an **ideal** gas.

An **ideal gas** is one that perfectly obeys all the assumptions of the kinetic theory of gases under all conditions of temperature and pressure.

Figure 9.34 The collisions between molecules are similar to the collisions between snooker balls. The collisions between the balls are elastic collisions as they bounce off each other.

Ideal gases do not exist! However, **real gases do come very close to ideal gas behaviour under two conditions:**

- At low pressure, when the molecules are widely spaced.
- At high temperatures, when the molecules are moving rapidly, preventing the forces between molecules from exerting an influence.

At very high pressures, gas molecules are forced much closer together. This means that we can no longer assume that the volume of the molecules can be ignored compared with the volume in which they move.

At high pressures and low temperatures, because the molecules are close together and moving slowly, the attractive forces between the molecules can be significant under these conditions.

However, under normal conditions (e.g. atmospheric pressure and a temperature of 20 °C) the behaviour of real gases comes very close to that of an ideal gas and, under these conditions, it is reasonable to take the assumptions of the kinetic theory of gases as validly applying to real gases.

In terms of the gas laws, an ideal gas may be described as one that obeys the gas laws exactly, e.g. an ideal gas would have zero volume at –273 °C (see Figure 9.25). This never occurs as real gases become liquids long before they reach this temperature. It should be noted that under the same conditions of temperature and pressure, non-polar molecules come closer to ideal behaviour than polar molecules, since the attractive forces are less in the case of non-polar molecules.

Boyle's Law, Charles' Law, Gay-Lussac's Law of Combining Volumes, and Avogadro's Law may all be explained in terms of the kinetic theory of gases.

Real gases differ from ideal gases because:

(i) forces of attraction and repulsion do exist between the molecules.

(ii) the volume of the molecules is not negligible.

Example 9.5

Question

Give two reasons why real gases depart from ideal behaviour. Under what conditions of temperature and pressure do real gases come closest to ideal behaviour? [LCH]

Answer

Real gases depart from ideal behaviour because:

(i) In an ideal gas, it is assumed that there are no forces of attraction between the molecules. In real gases, attractive forces exist between the molecules.

(ii) In an ideal gas, it is assumed that the molecules occupy negligible space. However, in real gases, the molecules occupy a small but definite space, which is not negligible at high pressure.

Real gases come closest to ideal behaviour at high temperature and low pressure.

9.6 The Ideal Gas Equation

Boyle's Law, Charles' Law and Avogadro's Law may be combined to give a mathematical relationship between the volume (V), pressure (p), temperature (T) and number of moles (n) of a gas.

Boyle's Law: $V \propto \frac{1}{p}$ at constant temperature.

Charles' Law: $V \propto T$ at constant pressure.

Avogadro's Law: $V \propto n$ at constant temperature and pressure.

Combining the above three relationships:

$$V \propto \left(\frac{1}{p}\right) T\, n$$

i.e. $V = R\frac{1}{p} T\, n$ where R is a constant of proportionality called the **Universal Gas Constant**.

Rearranging the above equation gives: $\boldsymbol{pV = nRT}$

This equation is called the **Ideal Gas Equation** or the **Equation of State for an Ideal Gas**. It is called the Equation of State because it tells us how, in going from one set of conditions in the gaseous state to another, the four variables V, P, T and n change.

The numerical value for R can be found by substituting experimental values into the equation. For example, we know that at s.t.p. one mole of any gas occupies a volume of 22.4 litres.

At s.t.p.

$T = 273$ K

$p = 1.013 \times 10^5$ Pa (normal atmospheric pressure)

$n = 1$ (for 1 mole of gas)

$V = 22.4\text{ L} = \frac{22.4}{1000} = 0.0224\text{ m}^3$

Note: We must convert litres to cubic metres. (There are 1000 litres in a cubic metre.) This is because we use metres in the units for pressure and we must, therefore, measure volume in cubic metres to keep the units consistent.

$$pV = nRT$$

$$R = \frac{pV}{nT}$$

$$= \frac{1.013 \times 10^5\ \text{Nm}^{-2} \times 0.0224\ \text{m}^3}{1\ \text{mole} \times 273\ \text{K}}$$

$$= 8.31\ \text{N m mol}^{-1}\ \text{K}^{-1}$$

Since a newton metre is also called a joule (symbol J), the above is often written as

$$R = 8.31\ \text{J mol}^{-1}\text{K}^{-1}$$

PV = nRT	***V:*** m^3	***R:*** J mol^{-1} K^{-1} (always given to you)
P: Pa	***n:*** mol	***T:*** K

When substituting into the equation $PV = nRT$, always ensure that the units of pressure are **pascals**, the units of volume are **cubic metres** and the units of temperature are **kelvins**.

Example 9.6

Question

Calculate the volume occupied by 10 g of oxygen gas at 25 °C and a pressure of 200 kPa.
[R = 8.31 J mol^{-1} K^{-1}]

Answer

p = 200 kPa = 200 × 10^3 Pa

V = ?

$$n = \frac{\text{Mass}}{\text{Rel. Molecular Mass}} = \frac{10}{32} = 0.31 \text{ mole}$$

R = 8.31 J mol^{-1} K^{-1}

T = 25 °C + 273 = 298 K

pV = nRT

$$V = \frac{nRT}{p}$$

$$= \frac{0.31 \times 8.31 \times 298}{200 \times 10^3} = 0.0038 \text{ m}^3$$

$$= 0.0038 \times 1000 \text{ litres}$$

$$= 3.8 \text{ L}$$

Alternative Method

This problem could also be solved using the Combined Gas Law.

Given	s.t.p.
V_1 = ?	V_2 = 22.4 L
p_1 = 200 kPa	p_2 = 100 kPa
T_1 = 25 °C + 273 = 298 K	T_2 = 0 °C + 273 = 273 K

Substitute into $\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$

$$\frac{200 \times V_1}{298} = \frac{100 \times 22.4}{273}$$

$$V_1 = \frac{100 \times 22.4 \times 298}{273 \times 200} = 12.23 \text{ L}$$

1 mole of O_2 occupies 12.23 L under the above conditions,

i.e. 32 g O_2 occupies 12.23 L

1 g O_2 occupies $\frac{12.23}{32}$ L

10 g O_2 occupies $\frac{12.23 \times 10}{32} = 3.8$ L

Answers: 3.8 L

Example 9.7

Question

A volatile liquid is one with a low boiling point. Calculate the relative molecular mass of a volatile liquid (X) from the following information: 0.20 g of X on vaporisation gave 40 cm^3 of vapour measured at 100 °C and a pressure of 100 kPa. [R = 8.31 J mol^{-1} K^{-1}]

Answer

p = 100 kPa = 100 × 10^3 Nm^{-2}

V = 40 cm^3= 40 × 10^{-6} m^3

n = ?

R = 8.31 J mol^{-1} K^{-1}

T = 100 °C + 273 = 373 K

pV = nRT

$$n = \frac{pV}{RT}$$

$$n = \frac{100 \times 10^3 \times 40 \times 10^{-6}}{8.31 \times 373} = 0.0013 \text{ moles}$$

i.e. 0.0013 mole = 0.20 gram

$$1 \text{ mole} = \frac{0.2}{0.0013} \text{ grams}$$

$$= 153.85 \text{ grams}$$

i.e. Relative molecular mass = 153.85

Answer: 153.85

EXAM TIP!

A common error among students when substituting into the equation $pV = nRT$ is to forget to convert volumes to m^3. As already explained, if you are given the volume in litres, you must divide by 1000 (i.e. × 10^{-3}) to convert to m^3. If you are given the volume in cm^3, you must divide by a million (i.e. × 10^{-6}) since there are a million cubic centimetres in a cubic metre.

Volume in cubic metres = volume in litres × 10^{-3}
Volume in cubic metres = volume in cm^3 × 10^{-6}

» Study Examples 9.8 and 9.9 in the online resources.

9.1 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 3 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 3

To measure the relative molecular mass of a volatile liquid using a conical flask

Introduction

The relative molecular mass of a compound may be found to a very high degree of accuracy with the aid of a mass spectrometer (Chapter 4). Using a mass spectrometer is the most accurate method of measuring the relative molecular masses of substances (solid, liquid or gas). However, mass spectrometers are not usually available in school laboratories. Therefore, we shall use a method first developed by a German chemist called Victor Meyer to measure the relative molecular mass of a volatile liquid. As previously mentioned, a **volatile liquid is one with a low boiling point**. This method is restricted to liquids that are volatile, as we will be using boiling water to vaporise the liquid and so the boiling point of the liquid must be below that of water.

In this method, we will fill a flask with the vapour of a volatile liquid at a known temperature. We will then find the mass of this vapour and, by calculation we will find the volume that this vapour would occupy at s.t.p. We will then calculate what the mass of 22 400 cm^3 of this vapour would be at s.t.p. This is the relative molecular mass of the liquid.

Key steps in procedure

The overall procedure may be divided into four stages.

1. **A flask is filled with the vapour of the volatile liquid at the temperature of boiling water and at atmospheric pressure.**

Procedure

- The mass of a clean, dry conical flask, a rubber band and a piece of aluminium foil are found using a laboratory balance.
- Approximately 10 cm^3 of the volatile liquid (e.g. propanone or cyclohexane) are poured into the conical flask.
- The aluminium foil is placed over the mouth of the flask and held in place using the rubber band.
- A very small pinhole is made in the aluminium foil cap.
- The flask is clamped in a large beaker of boiling water until all the volatile liquid has vaporised, Figure 9.35.
- The temperature of the boiling water is measured using a thermometer.
- The atmospheric pressure is measured using a barometer, Figure 9.36.

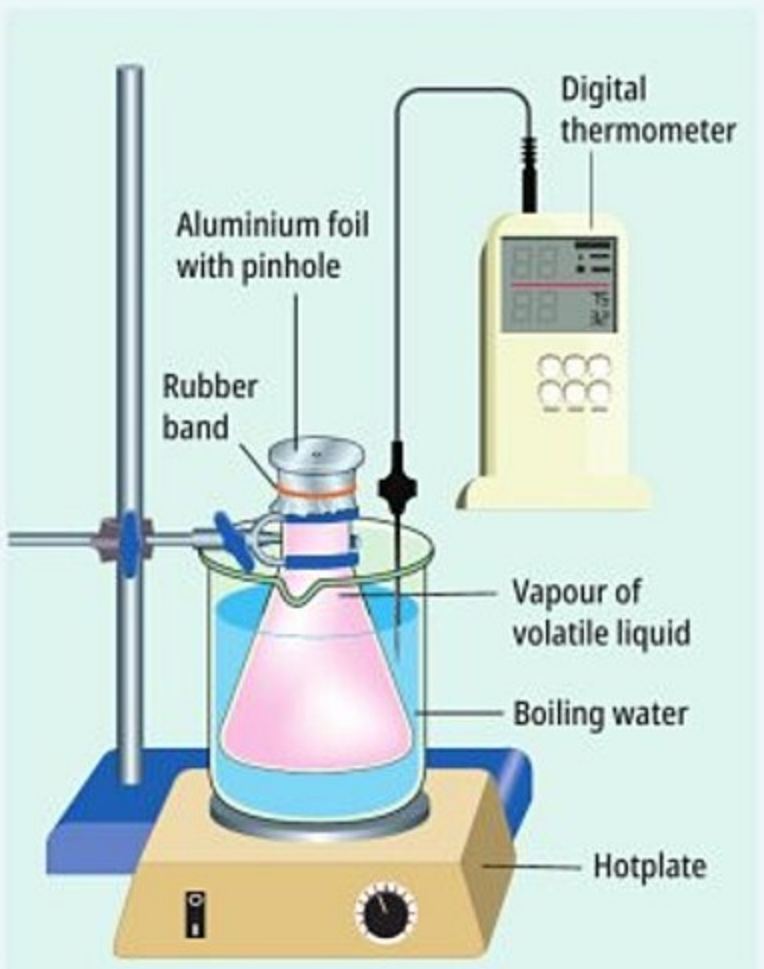


Figure 9.35 Apparatus to measure the relative molecular mass of a volatile liquid.

Figure 9.36 This datalogger is an easy way to measure the pressure of the atmosphere. The reading here is 101.5 kPa.

Observation

- After heating the conical flask for a while, all of the volatile liquid in the flask will have vaporised. No liquid will then be visible in the flask.

Explanation

- The purpose of the boiling water is to convert the volatile liquid to a vapour.
- The flask is left in the boiling water for about 8 minutes to ensure that all the liquid has vaporised.
- Although it appears that the flask is empty, it is now full of the vapour of the volatile liquid at 100 °C (the temperature of the boiling water). The temperature of the vapour is obtained by reading the temperature of the boiling water.
- The pinhole allows the air to be expelled from the flask, which is filled at this point with the vapour of the liquid.
- Any excess vapour escapes from the flask through the pinhole.
- The pressure of the vapour in the conical flask is the same as atmospheric pressure because the pinhole allows the vapour in the conical flask to be in contact with the air outside the conical flask, i.e. the conical flask is open to the atmosphere. The volume of volatile liquid added at the start of the experiment does not need to be accurately known since, when the liquid boils, the vapour of the liquid fills the flask and any excess vapour escapes through the pinhole.

2 The mass of the vapour of the volatile liquid that filled the flask is found.

Procedure

- The flask is removed from the boiling water and allowed to cool to room temperature.
- The outside of the flask and foil are dried.
- The flask, foil and rubber band are re-weighed.

Observation

- As the flask cools, droplets of liquid are seen forming inside the conical flask.

Explanation

- The vapour of the volatile liquid condenses back to a liquid as the flask is cooled.
- Air returns to fill the flask.
- The mass of the liquid whose vapour has filled the flask is calculated by subtracting the initial mass of the flask, foil and rubber band from the final mass of flask, foil, rubber band and condensed volatile liquid.

3 The volume occupied by the vapour of the volatile liquid is found.
Its volume is the same as that of the flask, which it had filled completely.

- The volume of the conical flask is found by filling it completely with water and pouring the water (in portions) into a 100 cm^3 graduated cylinder. As the volume of the water will exceed the capacity of the graduated cylinder, this will have to be repeated a number of times.

4 The results are recorded under the headings shown in your Laboratory Notebook. Using these results, you can now calculate the relative molecular mass of the volatile liquid. To assist you with calculations, some specimen results are shown in Example 9.10.

DIGITAL: A video of this experiment is available on FolensHIVE.

Example 9.10

Question

Some students carried out an experiment to measure the relative molecular mass of a volatile liquid. They filled a conical flask with the vapour of the liquid by placing the conical flask in boiling water at 100 °C. They obtained the following data:

Mass of empty flask, foil and rubber band	= 105.21 g
Mass of flask, foil, band and condensed liquid	= 106.30 g
Volume of conical flask	= 326 cm^3
Atmospheric pressure	= 98.5 kPa

Calculate the relative molecular mass of the volatile liquid.

Answer

Mass of empty flask, foil and rubber band	= 105.21 g
Mass of flask, foil, band and condensed liquid	= 106.30 g
Therefore, mass of condensed liquid	= 106.30 - 105.21 = 1.09 g
Volume of flask = volume of vapour	= 326 cm^3
Atmospheric pressure	= 98.5 kPa
Temperature of vapour in flask	= 100 °C + 273 = 373 K

Calculations

Given:

p = 98.5 kPa = 98.5×10^3 Pa

V = 326 cm^3 = 326×10^{-6} m^3

R = 8.3 J mol^{-1} K^{-1}

T = 100 °C = 100 + 273 = 373 K

Step 1

Calculate the number of moles of vapour present

$pV = nRT$

$$n = \frac{pV}{RT}$$

$$= \frac{98.5 \times 10^3 \times 326 \times 10^{-6}}{8.3 \times 373}$$

$$= 0.01$$

No of moles = 0.01

Step 2

Calculate the relative molecular mass

$$\text{No of moles} = \frac{\text{Mass}}{\text{Rel Molecular Mass}}$$

$$\text{Rel Molecular Mass} = \frac{\text{Mass}}{\text{No of moles}} = \frac{1.09}{0.01} = 109$$

Answer: Rel molecular mass = 109

Note: Do not be disappointed if you do not get exactly the right answer, as there are a number of possible sources of experimental error in this experiment:

- The laboratory balance may only read to an accuracy of one or two decimal places.
- A measuring instrument that is more accurate than the graduated cylinder could be used to measure the volume of the conical flask, e.g. a burette.
- It is very difficult to cover the entire flask with boiling water, so the vapour in the space near the top of the conical flask may not be at the temperature of the boiling water.
- The outside of the conical flask and foil may not be completely dry when carrying out the second weighing.

9.2 Teacher Demonstration Experiment

Teacher Demonstration Experiment 9.2

To verify the Ideal Gas Equation

To verify the Ideal Gas Equation, $pV = nRT$, you could use the same datalogging apparatus as was used to verify Boyle's Law.

1. Find the mass of an empty gas syringe.
2. Place a known volume of oxygen gas in the syringe.
3. By subtraction, find the mass of oxygen gas in the syringe.
4. Note the room temperature.
5. Attach the gas syringe to a pressure sensor, Figure 9.37.
6. Vary the volume of the gas by pushing down on the plunger. In each case, read the pressure corresponding to each volume.
7. Calculate the average value of pV.
8. Substitute the average value of pV into the left-hand side of the equation $pV = nRT$.
9. Now calculate the right hand side of the equation $pV = nRT$ by substituting in the measured value of n (number of moles of oxygen in the syringe), the value of T (room temperature) and the value of R.
10. Compare both sides of the equation. They should be equal!

Figure 9.37 Verifying the Ideal Gas Equation using a fixed quantity of oxygen gas in a gas syringe attached to a pressure sensor.

If the two sides of the equation are not exactly equal, this may be due to:

- **Experimental error:** The measurements that you have taken of pressure, volume, temperature and mass may be slightly inaccurate.
- **Non-ideal gas behaviour:** The Ideal Gas Equation hold for ideal gases. However, you are dealing with a real gas which can deviate from idea gas behaviour under condition of high pressure.

TEST YOURSELF: Attempt Questions 9.9–9.13 and W9.9–W9.24.

Study SEC exam question 9.10 and model answer in the online resources.

Summary What I should know

- The Kinetic Theory of Matter contains a number of assumptions about how substances behave under various conditions such as temperature, pressure and volume.
- Boyle's Law states that, at constant temperature, the volume of a fixed mass of gas is inversely proportional to its pressure.
- Charles' Law states that, at constant pressure, the volume of a fixed mass of gas is directly proportional to its temperature measured on the Kelvin scale.
- The Combined Gas Law (or General Gas Law) states that:

$$\frac{p_1V_1}{T_1} = \frac{p_2V_2}{T_2}$$

- Avogadro's Law states that equal volumes of gases contain equal numbers of molecules, under the same conditions of temperature and pressure.
- An ideal gas is one that perfectly obeys all the assumptions of the kinetic theory of gases under all conditions of temperature and pressure.
- The equation $pV = nRT$ is called the Ideal Gas Equation or the Equation of State for an Ideal Gas.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the Kinetic Theory of Matter.			
Discuss evidence for the Kinetic Theory of Matter.			
Summarise the relationships between volume, pressure and temperature of gases using Boyle's Law, Charles' Law, Gay-Lussac's Law of Combining Volumes and Avogadro's Law.			
Solve and interpret problems using the Combined Gas Law (General Gas Law) and the Ideal Gas Law (Equation of State for an Ideal Gas).			

Chapter review questions

9.1 **(a)** When using the term *particulate nature of matter*, what do chemists mean by the term *particle*?

(b) Explain with the aid of diagrams how the Kinetic Theory of Matter describes the arrangement of particles in solids, liquids and gases.

(c) What is meant by the melting point of a solid? Explain how the Kinetic Theory of Matter describes the process of melting.

(d) Distinguish between evaporation and boiling. Describe how the Kinetic Theory of Matter explains these two processes.

(e) Explain the term *Brownian motion* and describe how it may be demonstrated in the laboratory.

(f) Describe how the Kinetic Theory of Matter explains pressure in gases.

9.2 A student collected 75 cm^3 of hydrogen from the reaction between zinc and sulfuric acid at 20 °C and 900 kPa. What volume would this gas occupy at s.t.p.?

9.3 A sample of hydrogen of volume 100 cm^3 at a pressure of 1×10^5 Pa is compressed to 55 cm^3 at constant temperature. What is the new pressure of the gas?

9.4 A sample of helium gas occupies a volume of 5 litres at a pressure of 9.2×10^4 N m^{-2}. Calculate the volume that the gas will occupy if the pressure is increased to 1.01×10^5 N m^{-2} at constant temperature.

9.5 A chemical plant produced 2500 litres of ammonia at a pressure of 500 kPa and a temperature of 100 °C. A chemical engineer wished to store the ammonia at a pressure of 100 kPa and a temperature of 20 °C. What volume would the gas occupy at this new pressure and temperature?

9.6 50 cm^3 of nitrogen gas combine with 150 cm^3 of hydrogen gas to form 100 cm^3 of ammonia. Are these experimental facts in keeping with Gay-Lussac's Law of Combining Volumes? Explain your answer.

9.7 Given that the molar volume is 22.4 L at s.t.p, calculate the density of each of the following gases at s.t.p.: (a) ammonia, NH_3; (b) nitrogen, N_2; (c) chlorine, Cl_2; (d) methane, CH_4.

9.8 200 cm^3 of a certain gas at s.t.p. have a mass of 1 g. Calculate the relative molecular mass of the gas.

9.9 A student carried out an experiment to measure the relative molecular mass of a volatile liquid by filling a conical flask with the vapour of the liquid.

(a) What is meant by the term *volatile liquid*?

(b) Give an example of one volatile liquid that could be used in this experiment.

(c) Outline the main steps involved in carrying out this experiment.

(d) Calculate the relative molecular mass of the liquid from the following results:

Mass of empty flask, foil and band	= 108.41 g
Mass of flask, foil, band and condensed liquid	= 109.72 g
Volume of flask	= 332 cm^3
Atmospheric pressure	= 1.2×10^5 Pa
Temperature of vapour in flask	= 100 °C

(Take standard pressure as 1×10^5 Pa.)

9.10 State the assumptions of the kinetic theory of gases. What is an ideal gas? Under what conditions of temperature and pressure are deviations from ideal behaviour most marked? Which assumptions of the kinetic theory of gases are most likely to be false under these conditions?

9.11 Calculate the volume that 20 g of oxygen gas will occupy at 25 °C and 20 kPa pressure.

9.12 Calculate the relative molecular mass of a volatile liquid from the following information: 0.16 g of X on vaporisation gave 46 cm^3 of vapour measured at 100 °C and a pressure of 101.325 kPa.

9.13 A sample of chloroform of mass 0.495 g gave 127 cm^3 when vaporised at 98 °C at a pressure of 100.5 kPa. Calculate the relative molecular mass of chloroform.

10 Law of Conservation of Mass: Introducing Stoichiometry

OBJECTIVES

- To make students familiar with the work of Antoine Lavoisier and the Law of Conservation of Mass.
- To give students an understanding of the relationship between the amounts of reactants and products.
- To provide students with the opportunity to solve problems in the area of quantitative chemistry.

10.1 Introduction

The story of our next chemistry topic begins in France. It was here, in his laboratory in Paris, that Antoine Lavoisier (1743–1794) carried out chemistry experiments in which he was interested in taking accurate measurements. He convinced other chemists of the importance of taking accurate measurements when carrying out chemistry experiments. Lavoisier is considered to be one of the founders of modern **quantitative chemistry**, i.e. that branch of chemistry that focuses on amounts or quantities of substances that react together, Figure 10.1. He had hundreds of different measuring instruments in his laboratory.

Figure 10.1 Antoine Lavoisier took very accurate measurements of the masses and volumes of chemicals that take part in chemical reactions. This drawing shows him carrying a container of mercury for use in one of his most important experiments.

Many of his experiments involved gases and, by carefully measuring the masses of reactants and products, he made many important discoveries. For example, he discovered that air was made up of approximately 20% of oxygen gas. His careful measurements allowed him to work out the precise ratios in which substances react with each other. In particular, his experiments gave chemists a clear understanding of what happens when substances burn and this helped to debunk old theories about the process of burning.

We will now study one of the most important discoveries of Antoine Lavoisier.

10.2 Law of Conservation of Mass

In 1774 Lavoisier heated a known mass of mercury in a sealed glass container that had a limited supply of air. He observed that on heating the silvery mercury, it changed into a red powder called mercuric oxide (HgO), Figure 10.2.

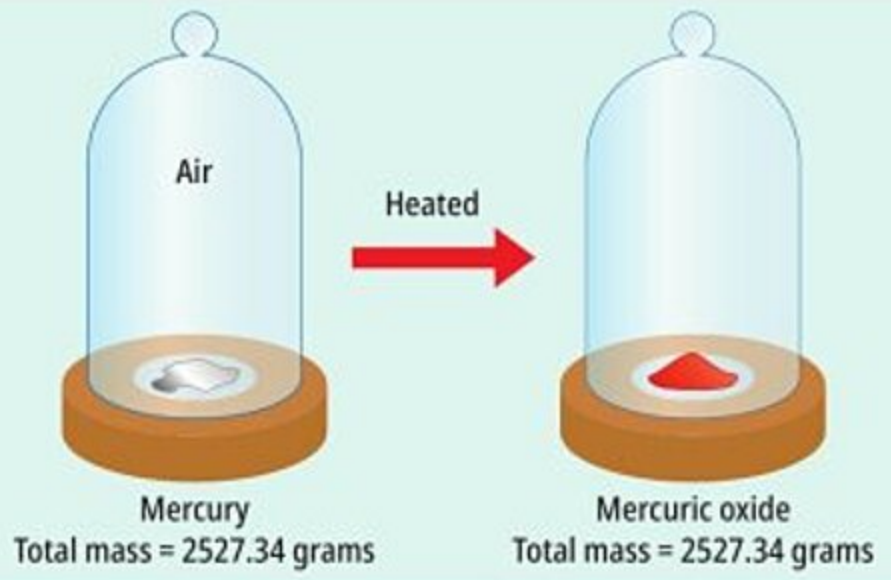


Figure 10.2 Diagrammatic representation of the experiment carried out by Lavoisier. He heated mercury in a sealed container and carefully measured the masses of reactants and products.

He carefully measured the mass of the container and its contents before and after heating it. He found that, even though the mercuric oxide looked different to the mercury, the mass of the entire container was the same before and after heating. He also noted that the mercuric oxide formed was heavier than the mercury.

The mass of the mercury had increased because it gained oxygen from the air:

Hg	+	$\frac{1}{2}O_2$	→	HgO
mercury		oxygen		mercuric oxide
100 g		8g		108 g

However, Lavoisier also found that the loss in mass of the oxygen in the container was exactly equal to the gain in mass of the mercury when it changed to mercuric oxide. In short, he discovered that there was no change in the total mass of reactants and products. Although the substances themselves had changes as a result of the reaction, the number of each type of atom remained the same and, therefore, there was no overall change in mass. In other words, he discovered that mass is conserved or kept the same in the chemical reaction. He repeated his experiment by heating various other elements (such as phosphorous, sulfur, tin and lead) in sealed containers of air. In all cases, he found that the total mass of the products was equal to the total mass of the reactants. He summarised his findings in the Law of Conservation of Mass.

The **Law of Conservation of Mass** states that when a chemical reaction occurs, the total mass of the reactants is always equal to the total mass of the products.

Total mass of reactants = Total mass of products

For example, if 12 grams of carbon combine with 32 grams of oxygen it is found that 44 grams of carbon dioxide are formed. Thus, atoms cannot simply 'disappear', i.e. all atoms present in the reactants must also be present in the products.

10.1 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 10.1 in the Student Laboratory Notebook.

Student Experiment No. 4

To Verify the Law of Conservation of Mass

You may recall that you carried out some experiments to verify the Law of Conservation of Mass at Junior Cycle level. We now study two experiments to verify this law. The Law of Conservation of Mass may be verified by carrying out the reaction between silver nitrate and chloride ions. We have already met this reaction in Chapter 5 when testing for the presence of chloride ions in aqueous solution.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

This experiment is shown in Figure 10.3. Full details of how to carry out this experiment are given in the Laboratory Notebook accompanying this textbook.

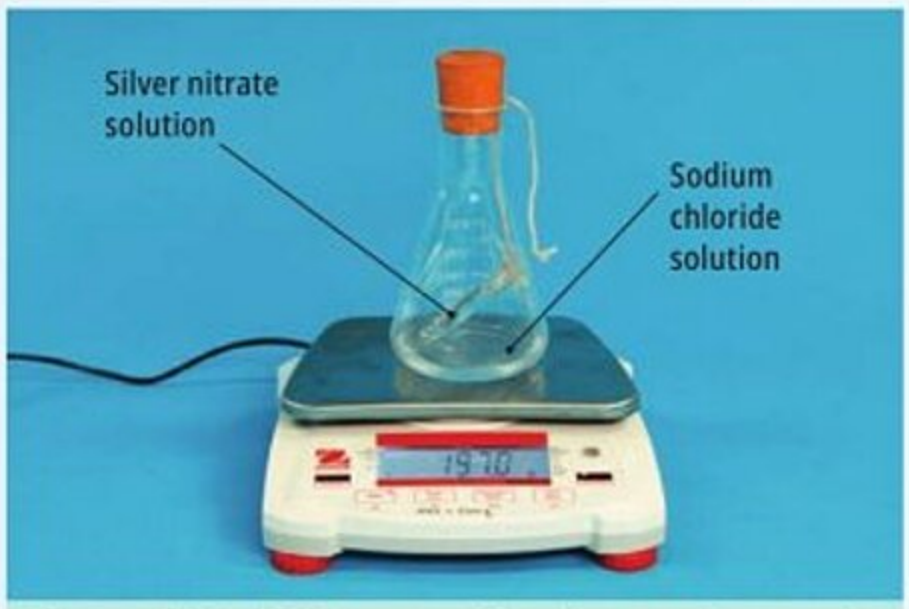


Figure 10.3a Before reaction, the total mass of the reactants and containers is 197.0 g.

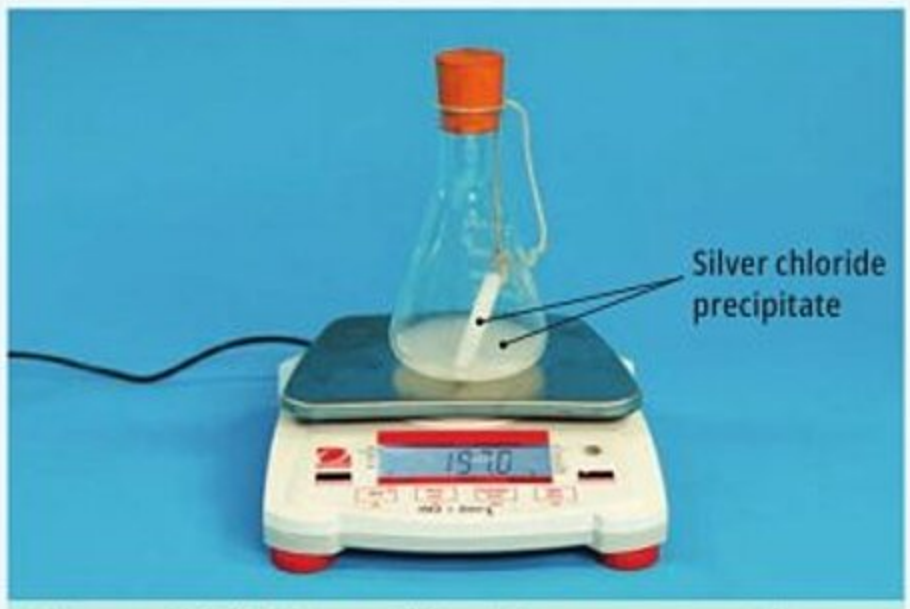


Figure 10.3b After mixing the reactants, silver chloride is formed. The total mass is still 197.0 g.

NOTE

Note that experiments to verify the Law of Conservation of Mass must be carried out in such a way that nothing can enter or escape when the reaction is taking place. This is often called a **closed system**. An example of a closed system is a flask with a tightly-fitting rubber stopper. The sealed container ensures that gases cannot escape or that materials cannot enter the flask to give false results.

The Law of Conservation of Mass may also be verified by studying the reaction that takes place when Alka-Seltzer tablets are added to water. The citric acid in the tablets reacts with the sodium hydrogencarbonate (also in the tablets) to produce carbon dioxide. We have also met this reaction in Chapter 5 when testing for the presence of hydrogencarbonate ions in aqueous solution:

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O$$

This experiment is shown in Figure 10.4. Full details of how to carry out this experiment are given in the Laboratory Notebook accompanying this textbook.

Figure 10.4a Before reaction, the total mass of the reactants and apparatus is 90.9 g.

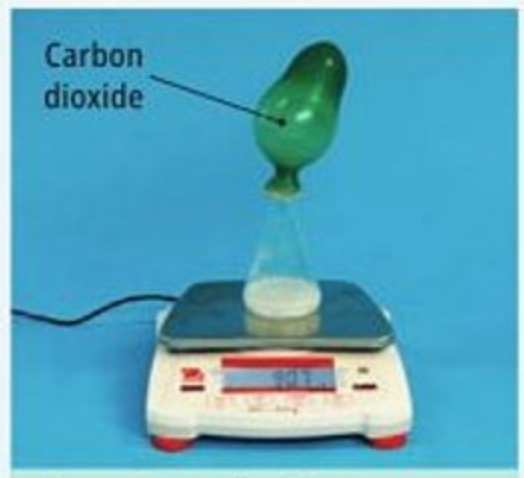


Figure 10.4b After mixing the reactants, carbon dioxide is formed. The total mass of the reactants and apparatus is 90.7 g.

Note: The slight discrepancy between the two masses is due to the buoyance effect of the balloon.

10.3 Physical and chemical changes: Law of Conservation of Mass

The Law of Conservation of Mass applies to all physical and chemical changes. You may recall at Junior Cycle that you studied both physical and chemical changes. To ensure that you are clear on the meaning of these terms, we now summarise some key points.

An example of a physical change is the melting of ice (solid to liquid) or the boiling of water (liquid to gas). In each case, no new substance is formed. Ice, water and steam are the same substance, i.e. they have the same chemical formula (H_2O). Some more examples of physical changes are shown in Figure 10.5. The Law of Conservation of Mass applies to all of these physical changes. For example, this may easily be shown by placing some ice cubes in a sealed container and finding the mass of the container and ice cubes. The same mass is observed when the ice cubes have melted.

Physical change may be compared to physical appearance. Physical appearance means how you look. You may change your physical appearance such as hair style or the clothes that you wear. Even though you look different, you are still the same person. Similarly, ice, water and steam all look different but they are still the same substance.

A **physical change** is a change that does not result in the formation of any new substance.

Physical properties are properties that can be observed without changing the substance into another substance.

Examples of physical properties are mass, shape, volume, density, melting point, and boiling point.

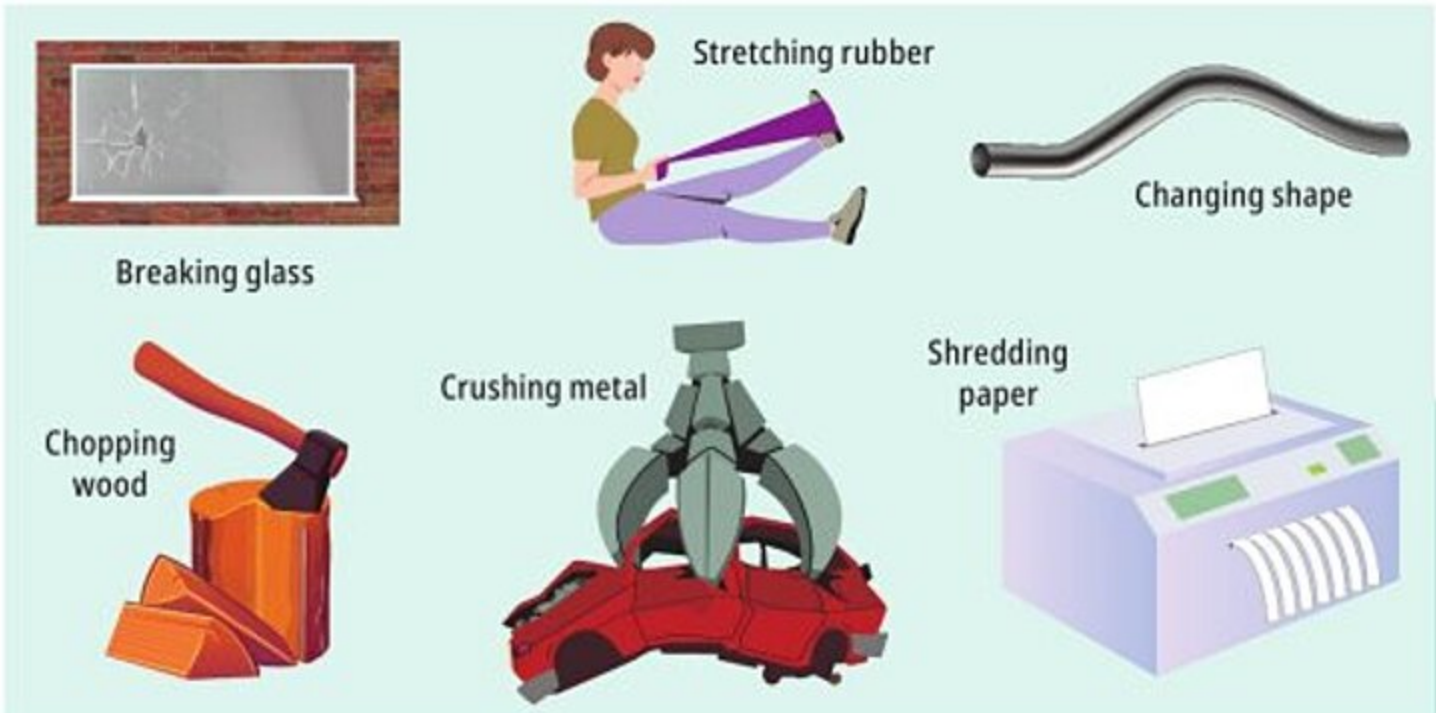


Figure 10.5 These changes are examples of physical changes because no new substance is formed. We are just changing the appearance of the substances.

In Chapter 5, when testing for the presence of various anions in aqueous solution, you carried out many chemical changes.

A **chemical change** is a change that results in the formation of one or more new substances.

- When a chemical change has taken place, we could also say that a **chemical reaction** has taken place. One of the most spectacular types of chemical reaction that take place is during a fireworks display. In this chemical reaction, a lot of heat, light and sound are produced. These are signs that a chemical reaction is taking place. The Law of Conservation of Mass applies to all these chemical changes.
- Other signs that a chemical reaction is taking place are that there may be a colour change, cloudiness may be observed, a smell may be detected or bubbles of gas may be formed, Figure 10.6.

Chemical properties describe how a substance **reacts** with other substances in a chemical reaction to form a new substance.

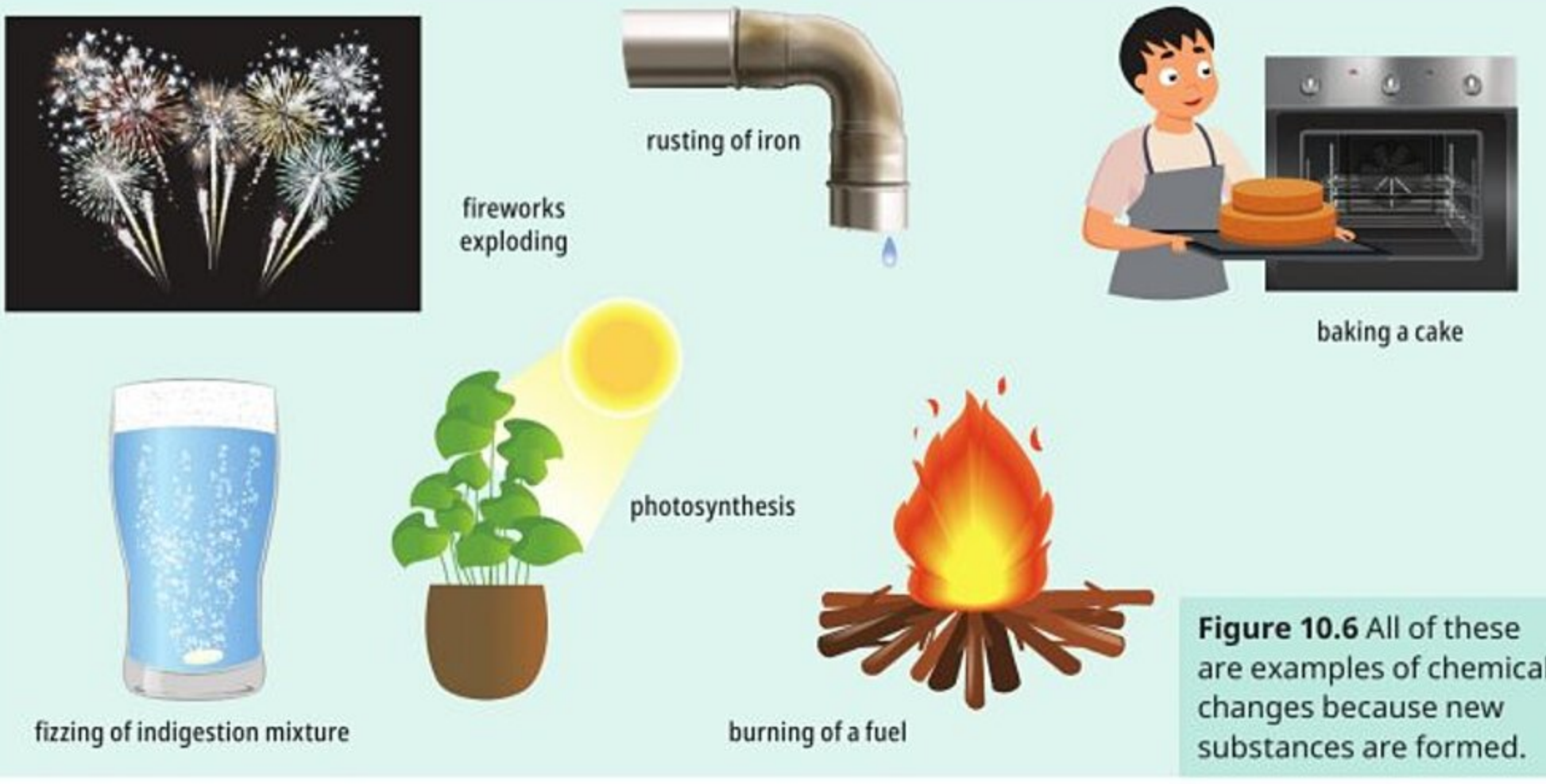


Figure 10.6 All of these are examples of chemical changes because new substances are formed.

We have already studied examples of chemical properties in Chapter 7, where we studied the reactions of groups of elements with water and oxygen.

The main differences between physical changes and chemical changes are summarised in Table 10.1. Many physical changes are easy to reverse, e.g. an ice cube that has melted can be frozen again. However, it would be very difficult to reverse the chemical reaction when Alka-Seltzer is added to water.

Physical change	Chemical change
1. No new substance is formed.	**1.** New substance is formed.
2. Usually no energy changes take place.	**2.** Energy changes take place: heat, light or sound are produced.
3. Easy to reverse.	**3.** Difficult to reverse.

Table 10.1 The differences between physical changes and chemical changes

TEST YOURSELF: Attempt Questions 10.1 and W10.1.

10.4 Law of Conservation of Mass and balancing chemical equations

The Law of Conservation of Mass provides the reason why chemical equations must always be balanced. You may recall learning about balanced chemical equations in your study of science at Junior Cycle level.

A **balanced chemical equation** has equal numbers of each type of atom on both sides of the equation.

If a chemical equation is not balanced, this would have to mean that some atoms have vanished or appeared out of nowhere – this, of course, does not happen. The Law of Conservation of Mass implies that there must be equal number of each type of atom on both sides of the equation. All that takes place when a chemical reaction occurs is that there is a rearrangement of atoms to form new substances.

Is the equation $2H_2 + O_2 \rightarrow 2H_2O$ balanced?

There are four hydrogen atoms on the left and four hydrogen atoms on the right of the equation. Also, there are two oxygen atoms on the left and two oxygen atoms on the right. Therefore, the equation is balanced. This may also be seen using Molymod models to illustrate the balanced equation, Figure 10.7.

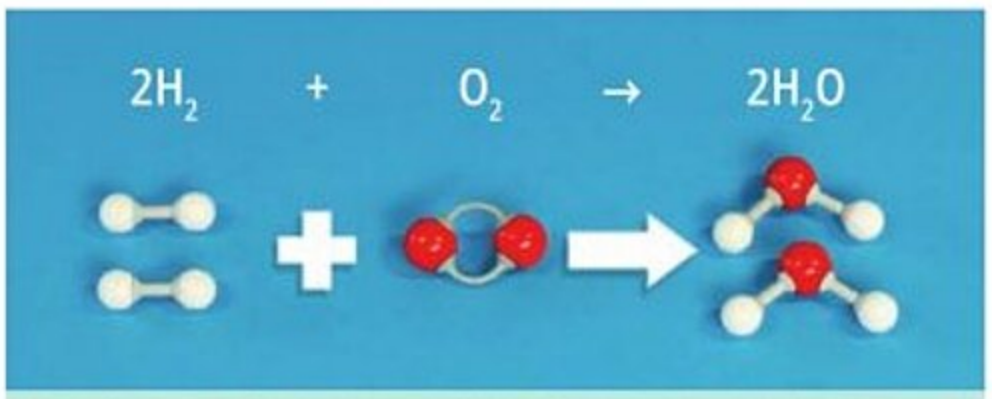


Figure 10.7 This equation is balanced, as the same number of each type of atom is present on both sides of the equation.

Let's look at another example to help you to understand the procedure involved in balancing an equation.

Example 10.1

Question

Balance the equation $CH_4 + O_2 \rightarrow CO_2 + H_2O$.

Answer

Step 1

Count the number of atoms of each element.

Left-hand side	Right-hand side
1 C atom	1 C atom
4 H atoms	2 H atoms
2 O atoms	3 O atoms

Step 2

Adjust the numbers in front of the formulas to ensure that equal numbers of each type of atom are on both sides of the chemical equation.

To get four H atoms on the right-hand side of the equation, put a '2' before the H_2O:

$CH_4 + O_2 \rightarrow CO_2 + 2H_2O$

The '2' before the H_2O tells us that there are two water molecules, consisting of four hydrogen atoms and two oxygen atoms. Thus, there are now four H atoms on the right-hand side. Therefore, the H atoms are balanced. Now check for the balancing of oxygen atoms.

Note that there are two oxygen atoms on the left-hand side of the equation. However, there are four oxygen atoms on the right-hand side (two in CO_2 and two in $2H_2O$). To get four oxygen atoms on the left-hand side, put a '2' before the O_2. This means we have two oxygen molecules, consisting of four oxygen atoms.

Left-hand side	Right-hand side
1 C atom	1 C atom
4 H atoms	4 H atoms
2 O atoms	4 O atoms

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$

Step 3

Recheck the balancing at the end. The number of atoms of each element on the left-hand side must be equal to the number of atoms of each element on the right-hand side.

Left-hand side	Right-hand side
1 C atom	1 C atom
4 H atoms	4 H atoms
4 O atoms	4 O atoms

The equation is now balanced. Balancing equations is made easy (and involves great fun!) with the use of *Molymod* molecular model kits. An illustration of the above balanced equation is shown in Figure 10.8.

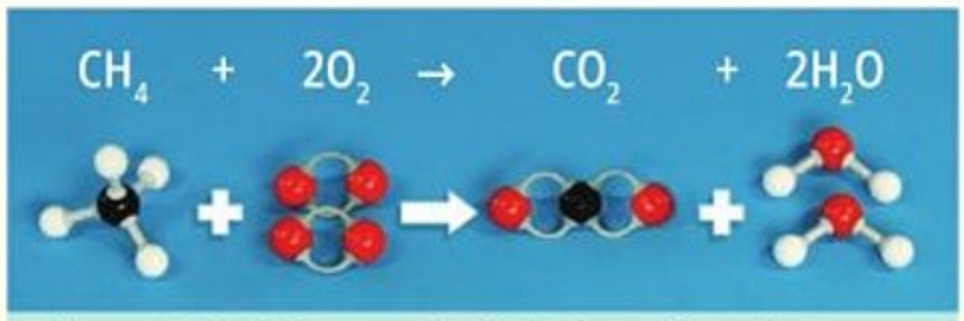


Figure 10.8 This equation is balanced, as the same number of each type of atom is present on both sides of the equation.

Note one very important point about balancing equations. **When balancing an equation, the formulas cannot be changed in any way**. The equation may only be balanced by putting numbers in front of the formulas. Thus you cannot change H_2O to H_4O as the compound H_4O does not exist!

You will become quite an expert at balancing chemical equations by working through the equations given in the questions at the end of this chapter and in the workbook.

The 'trial and error' method of balancing equations as outlined above is known as 'balancing by inspection'. In Chapter 14 we will study a more systematic method of balancing equations.

NOTE

While the lowest whole-number ratio is usually looked for in an exam, it may be acceptable to use fractions when balancing chemical equations. However, fractions smaller than ½ are usually not accepted. For example, the equation describing the reaction between hydrogen and oxygen can be written as:

$2H_2 + O_2 \rightarrow 2H_2O$

or $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$

This equation does not mean that half of a molecule of oxygen reacts. It simply means that the ratio between hydrogen and oxygen is 1 : ½ or 2 : 1.

TEST YOURSELF: Attempt Questions 10.2 and W10.2.

10.5 Applying the mole concept to balanced chemical equations

Consider the reaction between hydrogen gas and oxygen gas to form water. As already discussed, this reaction may be represented by the following balanced equation:

$$2H_2 + O_2 \rightarrow 2H_2O$$

We can interpret this equation in a number of ways. Firstly, it tells us that **two** hydrogen molecules react with **one** oxygen molecule to form **two** molecules of water.

$2H_2$	+	O_2	→	$2H_2O$
2 molecules		1 molecule		2 molecules

Secondly, we can interpret it in terms of the Avogadro number of molecules that react. If we multiply the number of molecules in the above balanced equation by the Avogadro constant, we now have:

$2H_2$	+	O_2	→	$2H_2O$
$2 \times 6 \times 10^{23}$ molecules		$1 \times 6 \times 10^{23}$ molecules		$2 \times 6 \times 10^{23}$ molecules

We have already seen that the amount of a substance that contains the Avogadro constant number of particles is called a **mole** of that substance. Therefore, the above equation may also be written as:

$2H_2$	+	O_2	→	$2H_2O$
2 moles		1 mole		2 moles

By converting moles to grams, we can also tell the masses of these substances that react and the amount of water that is formed.

$2H_2$	+	O_2	→	$2H_2O$
2 moles		1 mole		2 moles
i.e. (2×2) grams		$(16 + 16)$ grams		(2×18) grams
4 grams		**32 grams**		**36 grams**

This branch of chemistry is called stoichiometry.

Stoichiometry is the branch of chemistry that tells us the relationship between the amounts of reactants and products in a balanced chemical equation.

The word 'stoichiometry' comes from the Greek *stoicheoin* meaning 'element' and *metron* meaning 'measure'. Chemists need to have knowledge of stoichiometry because it enables them to decide on the quantities of reactants required to form a certain amount of product.

10.6 To calculate the percentage of each element in a compound

Very often it is important to be able to calculate the percentage of an element in a compound. For example, a farmer may wish to know the percentage of nitrogen in a particular fertiliser, Figure 10.9. A chemical engineer may need to calculate the percentage of a metal in an ore. The method of performing this type of calculation is shown in the examples that follow.

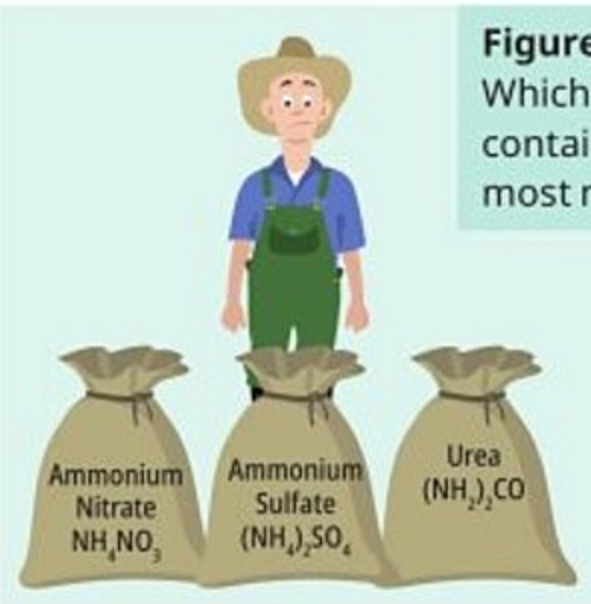


Figure 10.9 Which fertiliser contains the most nitrogen?

Example 10.2

Question

Ammonium nitrate, NH_4NO_3, is often used in fertilisers to supply nitrogen to the soil.

What is the percentage of nitrogen in ammonium nitrate? (H = 1, N = 14, O = 16)

Answer

Step 1

Calculate the relative molecular mass of ammonium nitrate.

Note that in one molecule of ammonium nitrate, there are two atoms of nitrogen, four atoms of hydrogen and three atoms of oxygen:

2 N = 2 × 14	= 28
4 H = 4 × 1	= 4
3 O = 3 × 16	= 48
Rel. Molecular Mass	= 80

Step 2

Calculate the percentage of nitrogen in NH_4NO_3.

$$\text{Percentage of N} = \frac{28}{80} \times 100 = 35\%$$

The percentage of nitrogen is 35%.

NOTE

In Example 10.2, we have given the values of relative atomic masses as rounded-off numbers. This will enable you to concentrate on the methods of solving problems in stoichiometry rather than being distracted by constantly referring to the SEC *Tables and Formulae* booklet. However, as previously mentioned, ensure you follow the instructions on the Leaving Certificate exam paper regarding the actual values of relative atomic masses to be used in solving problems.

Example 10.3

Question

Calcium oxide, CaO, is commonly called lime or quicklime. Calculate the percentage composition by mass of each element in calcium oxide, CaO. (O = 16, Ca = 40)

Answer

Step 1

Calculate the relative molecular mass of CaO.

Ca	= 40
O	= 16
Rel. Molecular Mass	= 56

Step 2

Calculate the percentage of both calcium and oxygen in CaO.

$$\text{Percentage of Ca} = \frac{40}{56} \times 100 = 71.43\%$$

$$\text{Percentage of O} = \frac{16}{56} \times 100 = 28.57\%$$

The percentage composition of CaO by mass is 71.43% Ca and 28.57% O.

TEST YOURSELF: Attempt Questions 10.3–10.4 and W10.3–W10.4.

10.7 To calculate the empirical formula of a compound given the percentage composition

We have already seen that a compound is represented by a chemical formula, e.g. a molecule of water is represented by the formula H_2O. This is called the **molecular formula** of the compound. It tells us that a molecule of water consists of two atoms of hydrogen and one atom of oxygen, i.e. the molecular formula tells us the actual number of atoms of each element present.

The **molecular formula** of a compound is a formula which shows the number and type of each atom present in a molecule of that compound.

There is another type of formula called the empirical formula.

The **empirical formula** of a compound is the formula showing the simplest whole-number ratio of the numbers of different atoms present in the molecule.

For example, the molecular formula of ethene is C_2H_4 but the empirical formula is CH_2. Some other examples of empirical and molecular formulas are shown in Table 10.2.

Compound	Molecular formula	Empirical formula
Water	H_2O	H_2O
Methane	CH_4	CH_4
Hydrogen peroxide	H_2O_2	HO
Acetylene	C_2H_2	CH
Butane	C_4H_{10}	C_2H_5
Benzene	C_6H_6	CH

Table 10.2 Examples of molecular and empirical formulas

Note that the molecular formula is a simple multiple of the empirical formula. Note also that in some cases, the molecular formula and the empirical formula are the same.

Molecular formula = empirical formula × n (where n = a whole number).

Example 10.5

Question

Glucose is the name of the sugar found in blood. The empirical formula of glucose is CH_2O. When the relative molecular mass of glucose is measured by a mass spectrometer, it is found to be 180. What is the molecular formula of glucose?

Answer

Step 1

Apply the formula relating molecular formula and empirical formula to determine n.

Molecular formula = empirical formula × n

$= (CH_2O) \times n$

i.e. $180 = (12 + 2 + 16) \times n$

$180 = 30 \times n$

$n = 6$

Step 2

Multiply empirical formula by n.

Therefore, molecular formula $= (CH_2O) \times 6$

$= C_6H_{12}O_6$

Answer: $C_6H_{12}O_6$

Chemists involved in quality control often need to have compounds analysed. One of the methods of doing this is to measure in the laboratory the percentage by mass of each of the elements present in the compound. Using this information, it is possible to work out the empirical formula of the compound, Figure 10.12. The method of calculation is illustrated in Example 10.6.

Figure 10.12 This apparatus is used to determine the empirical formula of a compound.

Example 10.6

Question

A compound containing only carbon, hydrogen and oxygen was found on analysis to contain 52.17% carbon, 13.04% hydrogen and 34.79% oxygen. What is the empirical formula of the compound? Using a mass spectrometer, it was found that the relative molecular mass of the compound was 92. What is the molecular formula? [H = 1, C = 12, 0 = 16]

The basic idea behind solving this problem is to realise that if we have 100 grams of the compound, 52.17 grams will be due to carbon atoms, 13.04 grams will be due to hydrogen atoms, and 34.79 grams will be due to oxygen atoms.

Step 1

Convert each of these masses to moles of atoms by dividing by the appropriate relative atomic mass. This will lead us to the mole ratio.

Step 2

Divide by the smallest number of moles to obtain the simplest whole number ratio, i.e. the empirical formula. Lay out your work in the form of a table as follows:

Element	Percentage	$\frac{\text{Percentage}}{\text{Rel. atomic mass}}$	Simplest ratio (divide by 2.17)
Carbon	52.17	$\frac{52.17}{12} = 4.35$	$\frac{4.35}{2.17} = 2$
Hydrogen	13.04	$\frac{13.04}{1} = 13\ 04$	$\frac{13.04}{2.17} = 6$
Oxygen	34.79	$\frac{3479}{16} = 2.17$	$\frac{2.17}{2.17} = 1$

smallest number

i.e. empirical formula = C_2H_6O

Step 3

Apply the equation relating molecular formula and empirical formula.

Molecular formula = empirical formula × n

$92 = (C_2H_6O) \times n$

$92 = [2\ (12) + 6\ (1) + 1\ (16)] \times n$

$92 = 46\ n$

$\frac{92}{46} = n$

$n = 2$

Therefore, molecular formula = $(C_2H_6O) \times 2 = C_4H_{12}O_2$

Answer: $C_4H_{12}O_2$

TEST YOURSELF: Attempt Questions 10.5–10.8 and W10.5–W10.7.

Note: In some cases, dividing by the smallest number obtained in the third column of the above table may not give whole numbers in the fourth column. To get whole numbers, it may be necessary to multiply by a certain factor. This is illustrated in Example 10.7.

CHEMISTRY LIVE » Study Example 10.7 in the online resources.

10.8 To calculate the empirical formula of a compound given the masses of reactants and products

In many cases, it is possible to calculate the formula of a compound by carefully measuring the masses of the substances involved in the reaction. Analysis that is based on the masses of compounds that react is usually referred to as **gravimetric analysis**. Some examples of this type of calculation now follow.

Example 10.8

Question

A student heated 1.02 g of copper powder in air and noted that that the brown copper powder turned black, Figure 10.13. It was found that the mass of black powder formed was 1.28 g. Assuming that the black powder is an oxide of copper, calculate the empirical formula of this oxide. (Cu = 63.5, 0 = 16)

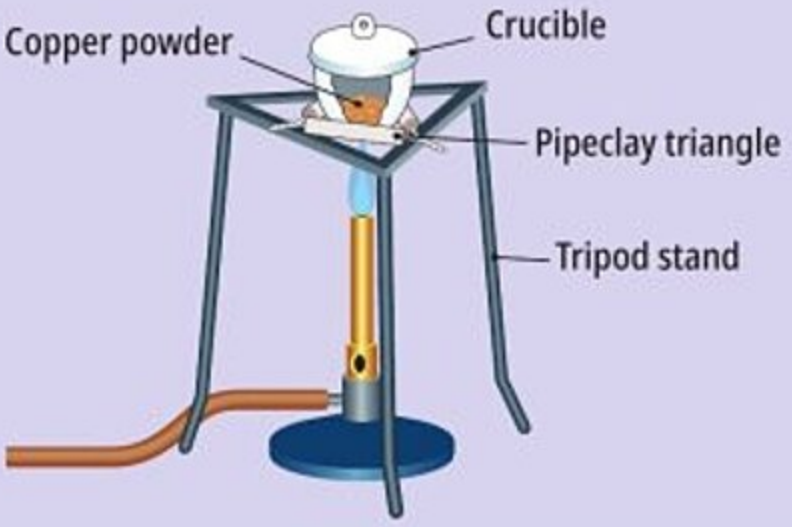


Figure 10.13 The brown copper powder turns black when heated. Copper is being converted into an oxide of copper. By measuring the mass of the copper metal and the mass of the oxide of copper that is formed, we can work out the empirical formula of the oxide of copper.

Answer

Step 1

Write out the word equation and insert the given masses.

copper + oxygen → copper oxide

1.02 g 1.28 g

Step 2

Apply the Law of Conservation of Mass to calculate the unknown mass.

mass of copper = 1.02 g

mass of copper oxide formed = 1.28 g

∴ mass of oxygen in copper oxide = 1.28 – 1.02 = 0.26 g

Step 3

Calculate the number of moles of copper atoms and oxygen atoms.

No. of moles of copper atoms in copper oxide = $\frac{1.02}{63.5} = 0.016$

and no. of moles of oxygen atoms in copper oxide = $\frac{0.26}{16} = 0.016$

Step 4

Divide by the smallest number of moles to obtain the simplest whole number ratio.

In this case, the mole ratios are the same.

Ratio of Cu : O = 0.016 : 0.016 = 1 : 1

Therefore, empirical formula of copper oxide is CuO.

Thus, the following reaction has occurred:

$Cu + \frac{1}{2} O_2 \rightarrow CuO$

Answer: CuO

Example 10.9

Question

In an experiment to determine the formula of an oxide of copper, hydrogen gas was passed over the heated oxide. It was found that 5.4 g of the oxide gave 4.8 g of copper. Calculate the empirical formula of the oxide. (Cu = 63.5, O = 16)

Answer

Step 1

Write out the word equation and insert the given masses.

copper oxide + hydrogen → copper

5.4 g 4.8 g

Step 2

Apply the Law of Conservation of Mass to calculate the unknown mass.

mass of copper oxide = 5.4 g

mass of copper in copper oxide = 4.8 g

Therefore, mass of oxygen in copper oxide = 5.4 – 4.8 = 0.6 g

Step 3

Calculate the number of moles of copper atoms and oxygen atoms.

$$\text{No. of moles of copper atoms in copper oxide} = \frac{4.8}{63.5} = 0.076 \text{ moles}$$

$$\text{No. of moles of oxygen atoms in copper oxide} = \frac{0.6}{16} = 0.038 \text{ moles}$$

Step 4

Divide by the smallest number of moles to obtain the simplest whole number ratio.

Ratio of Cu : O = 0.076 : 0.038

= 2 : 1

Therefore, the empirical formula of copper oxide is Cu_2O.

Thus, the following reaction has occurred:

$Cu_2O + H_2 \rightarrow 2Cu + H_2O$

Answer: Cu_2O

Note that there are two oxides of copper, Figure 10.14. CuO is called copper(II) oxide. Cu_2O is called copper(I) oxide.

Figure 10.14 The formula of the black copper(II) oxide is CuO. The formula of the red copper(I) oxide is Cu_2O.

Example 10.10

Question

Sodium sulfate is commonly called Glauber's salt and is used as a laxative in many medicines, Figure 10.15. A student heated 1.61 g of hydrated sodium sulfate crystals, $Na_2SO_4.xH_2O$, in a crucible over a Bunsen burner until no further loss in mass occurred. It was found that 0.71 g of the anhydrous salt was obtained. Calculate the formula of the hydrated salt. (H = 1, O = 16, Na = 23, S = 32).

Figure 10.15 Sodium sulfate is commonly called Glauber's salt after the pharmacist who discovered it.

Answer

Step 1

Write out the equation and insert the given masses.

Heating the crystals converts the hydrated sodium sulfate to anhydrous sodium sulfate.

$$Na_2SO_4.xH_2O \rightarrow Na_2SO_4 + xH_2O$$
$$1.61\ g \qquad 0.71\ g$$

Step 2

Apply the Law of Conservation of Mass to calculate the unknown mass.

Mass of hydrated crystals = 1.61 g

Mass of anhydrous salt = 0.71 g

Therefore, mass of water = 1.61 – 0.71 = 0.90 g

Step 3

Calculate the number of moles of Na_2SO_4 and water.

Rel. Molecular Mass $Na_2SO_4 = 2(23) + 32 + 4(16) = 142$

$$\text{No. of moles of } Na_2SO_4 = \frac{0.71}{142} = 0.005$$

$$\text{No. of moles of water} = \frac{0.90}{18} = 0.05$$

Step 4

Divide by the smallest number of moles to obtain the simplest whole number ratio.

Therefore, ratio $Na_2SO_4 : H_2O = 0.005 : 0.05$

$= 1 : 10$

i.e. $x = 10$

i.e. formula of hydrated salt is $Na_2SO_4.10H_2O$

Answer: $Na_2SO_4.10H_2O$

TEST YOURSELF: Attempt Questions 10.9–10.12 and W10.8–W10.10.

Study Example 10.11 in the online resources.

10.9 Calculating masses of reactants and products from balanced chemical equations

We have already seen that a balanced equation tells us the amounts of substances that react together and the amounts of products formed. This type of information is very useful for chemists and enables them to perform calculations to determine the amounts of reactants needed to produce a certain amount of product. We now consider some of these types of calculations.

Example 10.12

Question

Magnesium reacts with oxygen to produce magnesium oxide, Figure 10.16, according to the equation:

$2Mg + O_2 \rightarrow 2MgO$

If a student burns 9 g of magnesium in excess oxygen (i.e. there is plenty of oxygen present to ensure that **all** of the magnesium reacts), what mass of magnesium oxide will be formed? (Mg = 24, 0 = 16)

Figure 10.16 The reaction of magnesium with oxygen in the air is one of the reactions that take place when sparklers are lit.

Answer

Step 1

Write down the given equation and circle what <u>we know</u> and what <u>we want to know</u>.

$(2Mg) + O_2 \rightarrow (2MgO)$

Step 2

Make a shortened version of the equation and put in the amounts.

2Mg	→ 2MgO
2 moles	→ 2 moles
2(24) g	→ 2 (24 + 16) g
i.e. 48 g Mg	→ 80 g MgO

Step 3

Determine the mass of MgO formed.

Therefore, 1 g Mg $\rightarrow \frac{80}{48}$ g MgO

Therefore, 9 g Mg $\rightarrow \frac{9 \times 80}{48}$ g MgO

= 15 g MgO

Answer: 15 g of magnesium oxide will be formed from 9 g of Mg.

Example 10.13

Question

Lime (calcium oxide) is manufactured in a lime kiln, Figure 10.17, by heating limestone (calcium carbonate) to bring about the following reaction:

$CaCO_3 \rightarrow CaO + CO_2$

Calculate the amount of lime that could theoretically be obtained by heating 5 kg of limestone.
(C = 12, Ca = 40, O = 16)

Figure 10.17 Limestone is converted into lime by heating the limestone in this lime kiln. The lime produced will be used to make cement.

Answer

Step 1

Convert kilograms to grams.

This problem is fairly straightforward if one remembers to convert kilograms to grams.

5 kg = 5000 g

Step 2

Write down the given equation and circle what we know and what we want to know.

$CaCO_3 \rightarrow CaO + CO_2$

Step 3

Make a shortened version of the equation and put in the amounts.

$CaCO_3$	$\rightarrow$ CaO
1 mole	$\rightarrow$ 1 mole
[40 + 12 + 3(16)] g	$\rightarrow$ [40 + 16] g
i.e. 100 g $CaCO_3$	$\rightarrow$ 56 g CaO

Step 4

Calculate the mass of CaO obtained.

$1 \text{ g } CaCO_3 \rightarrow \frac{56}{100} \text{ g CaO}$

$\therefore 5000 \text{ g } CaCO_3 \rightarrow \frac{5000 \times 56}{100} \text{ g CaO}$

$= 2800 \text{ g}$

$= 2.8 \text{ kg}$

Answer: 2.8 kg of lime will be obtained from 5 kg limestone.

NOTE

Unit analysis

In solving problems in stoichiometry, it is important that you pay close attention to the units. This is commonly called **unit analysis**. For instance, in Example 10.14 we had to convert kilograms to grams by multiplying by 1000 (or 1×10^3). Similarly, if the problem was given in tonnes, we would have to convert tonnes to grams by multiplying by 1×10^6. Other examples of unit analysis are where we convert number of grams to number of moles, and where we convert number of moles to number of molecules, as shown in the above examples.

TEST YOURSELF:
Attempt Questions 10.13–10.15 and W10.11–W10.12.

10.10 Calculating volumes of gases from balanced chemical equations

When performing calculations on balanced equations which involve gases, chemists usually measure the volume of a gas rather than just its mass. We have already learned that one mole of any gas occupies a volume of 22.4 litres at s.t.p. We use this fact to calculate the volumes of gases used up or formed in chemical reactions. In calculating volumes of gases from balanced chemical equations, we follow the same procedure as shown in the following examples.

Example 10.14

Question

Carbon dioxide is formed when carbon is burned in oxygen, Figure 10.18, according to the equation:

$C + O_2 \rightarrow CO_2$

What volume of carbon dioxide (at s.t.p.) is formed when 30 g of carbon are burned in excess oxygen?

Figure 10.18 The burning of large carbon electrodes plays an important role in the manufacture of steel in the electric arc furnace.

Answer

Step 1

Write down the given equation and circle what we know and what we want to know.

$C + O_2 \rightarrow CO_2$

Step 2

Make a shortened version of the equation and put in the amounts.

$C \rightarrow CO_2$

1 mole $\rightarrow$ 1 mole

30g $\rightarrow$?

Step 3

Calculate the volume of CO_2 obtained.

$C \rightarrow CO_2$

1 mole $\rightarrow$ 1 mole

12 g C $\rightarrow$ 22.4 L of CO_2 at s.t.p.

1 g C $\rightarrow \frac{22.4}{12}$ L of CO_2

30 g C $\rightarrow \frac{30 \times 22.4}{12}$ L of CO_2

= 56 L of carbon dioxide.

Answer: 56 litres.

» Study Example 10.15 in the online resources.

SEC exam question 10.16

Nitric acid may be used to produce calcium ammonium nitrate ($5Ca(NO_3)_2.NH_4NO_3.10H_2O$).

This compound is used as a fertiliser and is commonly known as CAN.

When dissolved in water, CAN dissociates into the calcium ion (Ca^{2+}), the ammonium ion (NH_4^+), and the nitrate ion (NO_3^-).

Calculate the percentage by mass of nitrogen in calcium ammonium nitrate.

Calcium ammonium nitrate (CAN) is an unusual salt but do not worry as you do not need to know anything about the salt itself. You just need to be able to perform the required calculation.

This type of salt is often called a double salt, as its crystals actually contain two salts. One salt is calcium nitrate [$Ca(NO_3)_2$] and the other salt is ammonium nitrate (NH_4NO_3). The '5' at the beginning of the formula tells you that for every one mole of ammonium nitrate in the crystal, there are five moles of calcium nitrate in the crystal.

Step 1.

Work out the relative molecular mass of calcium ammonium nitrate

$5Ca(NO_3)_2.NH_4NO_3.10H_2O$

$5Ca = 5 \times 40.08 = 200.40$

$12N = 12 \times 14.01 = 168.12$

$43O = 43 \times 16.00 = 688.00$

$24H = 24 \times 1.008 = 24.192$

$M_r = 1080.712$

Step 2.

Calculate the percentage by mass of nitrogen in calcium ammonium nitrate

$$\text{Percentage of N} = \frac{168.12}{1080.712} \times 100 = 15.56\%$$

Answer 15.56%

TEST YOURSELF: Attempt Questions 10.16–10.18 and W10.13–W10.26

Summary What I should know

- The Law of Conservation of Mass states that when a chemical reaction occurs the total mass of the reactants is always equal to the total mass of the products.
- A physical change is a change that does not result in the formation of any new substance.
- A chemical change is a change that results in the formation of one or more new substances.
- A balanced chemical equation has equal numbers of each type of atom on both sides of the equation.
- Balanced chemical equations can be interpreted in terms of molecules, moles, grams and volumes of gases.
- Stoichiometry is the branch of chemistry that tells us the relationship between the amounts of reactants and products in a balanced chemical equation.
- The molecular formula of a compound is a formula which shows the number and type of each atom present in a molecule of that compound.
- The empirical formula of a compound is the formula showing the simplest whole-number ratio of the numbers of different atoms present in the molecule.
- Molecular formula = empirical formula × n (where n = a whole number).
- The empirical formula of a compound can be calculated from the percentage composition and also from the masses of reactants and products in the reaction to form the compound.
- Masses of reactants and products as well as volumes of gases can be calculated from balanced chemical equations.

Learning outcomes

At the end of this chapter, I should be able to:			
State the Law of Conservation of Mass and describe an experiment to verify it.	⬡	⬡	⬡
Distinguish between physical and chemical changes.	⬡	⬡	⬡
Balance chemical equations.	⬡	⬡	⬡
Calculate the percentage of each element in a compound.	⬡	⬡	⬡
Calculate the empirical formula of a compound given the percentage composition or given masses of reactants and products in the reaction to form the compound.	⬡	⬡	⬡
Calculate the masses of reactants and products from balanced chemical equations.	⬡	⬡	⬡
Calculate volumes of gases from balanced chemical equations.	⬡	⬡	⬡

Chapter review questions

When answering these questions, use the following values of relative atomic masses:
H = 1, He = 4, Li = 7, C = 12, N = 14, O = 16, F = 19, Na = 23, Mg = 24, Al = 27, Si = 28, P = 31, S = 32, Cl = 35.5, K = 39, Ca = 40, Cr = 52, Mn = 55, Fe = 56, Cu = 63.5, Zn = 65, Br = 80, Ag = 108, Sn = 119, I = 127, Pb = 207.

10.1 **(a)** The French chemist Antoine Lavoisier was very interested in taking accurate measurements when carrying out chemistry experiments. What name is given to this type of chemistry?

(b) State the Law of Conservation of Mass.

(c) With the aid of a labelled diagram, describe an experiment to verify the Law of Conservation of Mass.

(d) Explain the term *closed system* as it applies to verifying the Law of Conservation of Mass.

(e) Why is it necessary to have a closed system when verifying the Law of Conservation of Mass?

10.2 Balance each of the following equations.

(a) $NO + O_2 \rightarrow NO_2$

(b) $Fe + O_2 \rightarrow Fe_3O_4$

(c) $Al + Fe_2O_3 \rightarrow Al_2O_3 + Fe$

(d) $P + O_2 \rightarrow P_2O_5$

(e) $Al + Cl_2 \rightarrow AlCl_3$

(f) $Mg(OH)_2 + HCl \rightarrow MgCl_2 + H_2O$

(g) $HNO_3 + Ca(OH)_2 \rightarrow Ca(NO_3)_2 + H_2O$

(h) $Na_2CO_3 + HCl \rightarrow NaCl + H_2O + CO_2$

(i) $N_2 + O_2 \rightarrow NO$

(j) $K + H_2O \rightarrow KOH + H_2$

(k) $AgNO_3 + HCl \rightarrow AgCl + HNO_3$

(l) $BaCl_2 + Na_2SO_4 \rightarrow NaCl + BaSO_4$

(m) $AsCl_3 + 3H_2O \rightarrow H_3AsO_3 + HCl$

(n) $FeCl_3 + NaOH \rightarrow Fe(OH)_3 + NaCl$

(o) $C_8H_{18} + O_2 \rightarrow CO_2 + H_2O$

Percentage Composition

10.3 Calculate the percentage by mass of each element in the following compounds:

(a) magnesium oxide, MgO

(b) aluminium oxide, Al_2O_3

(c) magnesium sulfate, $MgSO_4$

(d) limestone, $CaCO_3$

(e) sodium chloride, $NaCl$

(f) ammonium sulfate, $(NH_4)_2SO_4$

(g) ethanedioic acid, $(COOH)_2$

(h) ethanoic acid, CH_3COOH

(i) lead nitrate, $Pb(NO_3)_2$

(j) potassium hydrogencarbonate, $KHCO_3$

10.4 Which of the three fertilisers – ammonium nitrate [NH_4NO_3], ammonium sulfate, [$(NH_4)_2SO_4$] and urea [$(NH_2)_2CO$] – contains the highest percentage of nitrogen?

Empirical and Molecular Formulas

10.5 Write down the empirical formulas of the following compounds: C_6H_{12}, $C_2H_4O_2$, $C_3H_6O_3$.

10.6 Urea is the name of a substance found in urine. The empirical formula of urea is N_2H_4CO. The relative molecular mass of urea, when measured by a mass spectrometer, is found to be 60. What is the molecular formula of urea? Draw a Lewis diagram for a molecule of urea.

10.7 Calculate the empirical formulas of each of the compounds containing:

(a) nitrogen 47%, oxygen 53%

(b) nitrogen 30.5%, oxygen 69.5%

(c) carbon 75%, hydrogen 25%

(d) carbon 85.7%, hydrogen 14.3%

(e) iron 34.5%, chlorine, 65.5%

(f) carbon 92.3%, hydrogen 7.7%

(g) sulfur 40%, oxygen 60%

(h) sulfur 50%, oxygen 50%

(i) potassium 40.2%, chromium 26.9%, oxygen 32.9%

(j) potassium 26.6%, chromium 35.4%, oxygen 38%

(k) copper 34.6%, iron 30.5%, sulfur 34.9%

Chapter review questions

10.8 A sample of washing soda was analysed and found to have the following composition: carbon 4.2%, oxygen 16.8%, sodium 16.1%, water of crystallisation 62.9%. Determine the empirical formula of washing soda.

Gravimetric Analysis

10.9 When 2.0 g of calcium were completely burnt in oxygen, 2.8 g of calcium oxide was obtained. What is the empirical formula of calcium oxide?

10.10 When 2.70 g of aluminium combined with oxygen it was found that 5.10 g of aluminium oxide was formed. What is the empirical formula of aluminium oxide?

10.11 A student heated 4.10 g of hydrated magnesium sulfate, $MgSO_4.xH_2O$, and found that 2.00 g of the anhydrous salt remained. Calculate the degree of hydration in the hydrated salt, i.e. calculate the value of *x*.

10.12 When 5.30 g of a metal oxide, MO, was reduced, 4.24 g of the metal was formed. Calculate the relative atomic mass of M.

Calculations from balanced equations

10.13 Iron reacts with chlorine to form iron(III) chloride according to the equation:

$2Fe + 3Cl_2 \rightarrow 2FeCl_3$

What mass of iron(III) chloride can be obtained from 20 g of iron?

10.14 The following reaction occurs during the manufacture of sulfuric acid:

$2SO_2 + O_2 \rightarrow 2SO_3$

Assuming that the sulfur dioxide is completely converted to sulfur trioxide, calculate the mass of sulfur trioxide that could be produced from 200 g of sulfur dioxide.

10.15 When glucose undergoes fermentation, ethanol and carbon dioxide are formed. This process may be represented by the equation:

$C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$

Assuming that the reaction goes to completion, calculate the mass of ethanol that could be obtained from 25 g of glucose.

Volumes of gases

10.16 Calculate the volume of carbon dioxide formed at s.t.p. when 2.5 g of limestone (calcium carbonate) is heated. The reaction that occurs is: $CaCO_3 \rightarrow CaO + CO_2$

10.17 Baking powder contains sodium hydrogencarbonate, $NaHCO_3$. On heating this substance, it is decomposed to form carbon dioxide which causes the dough to rise. The equation for the reaction is:

$2NaHCO_3 \rightarrow CO_2 + Na_2CO_3 + H_2O$

Calculate the mass of sodium hydrogencarbonate that would be needed to form 800 cm^3 of carbon dioxide at s.t.p.

10.18 Oxygen is prepared by the decomposition of hydrogen peroxide according to the equation:

$2H_2O_2 \rightarrow 2H_2O + O_2$

Calculate the volume of oxygen formed at s.t.p. by the decomposition of a solution containing 21 g of hydrogen peroxide.

11 Acids and Bases

11.1 Introduction

OBJECTIVES

- To introduce students to commonly used substances classified as acids or bases.
- To give students an understanding of two important theories of acids and bases.
- To ensure that students know the main types of chemical reactions involving acids and bases.
- To give students experience of predicting products of reactions involving acids and bases and balancing chemical equations.

You may recall that we met the word 'acid' at Junior Cycle science level. We learned that the word 'acid' comes from the Latin word **acidus** meaning 'sour'. If you study Figure 11.1 you will recognise many substances with a sour or sharp taste. For example, fizzy drinks contain an acid called carbonic acid. Vinegar contains an acid called acetic acid (also called ethanoic acid).

Many people think of acids as dangerous substances. It is true that some acids can be dangerous and must be handled with care (e.g. the sulfuric acid in a car battery). However, as is clear from Figure 11.1, many other acids are part of our diet. For example, we find acetic acid (ethanoic acid) in vinegar, citric acid in oranges and lemons, and carbonic acid in fizzy drinks. Rainwater also contains carbonic acid and, therefore, is slightly acidic. Also, some acids are necessary to keep us healthy: vitamin C is an acid called ascorbic acid, soap contains the salt of an acid called stearic acid, and benzoic acid is used as a food preservative.

You may also remember that we met the word 'base' in studying chemistry at Junior Cycle level. A base is often called the 'chemical opposite' of an acid. Some examples of common bases are shown in Figure 11.2.

One of the reasons why bases are called the 'chemical opposites' of acids is because they have the opposite effect to acids on litmus paper. While acids turn blue litmus paper red, bases turn red litmus paper blue, Figure 11.3.

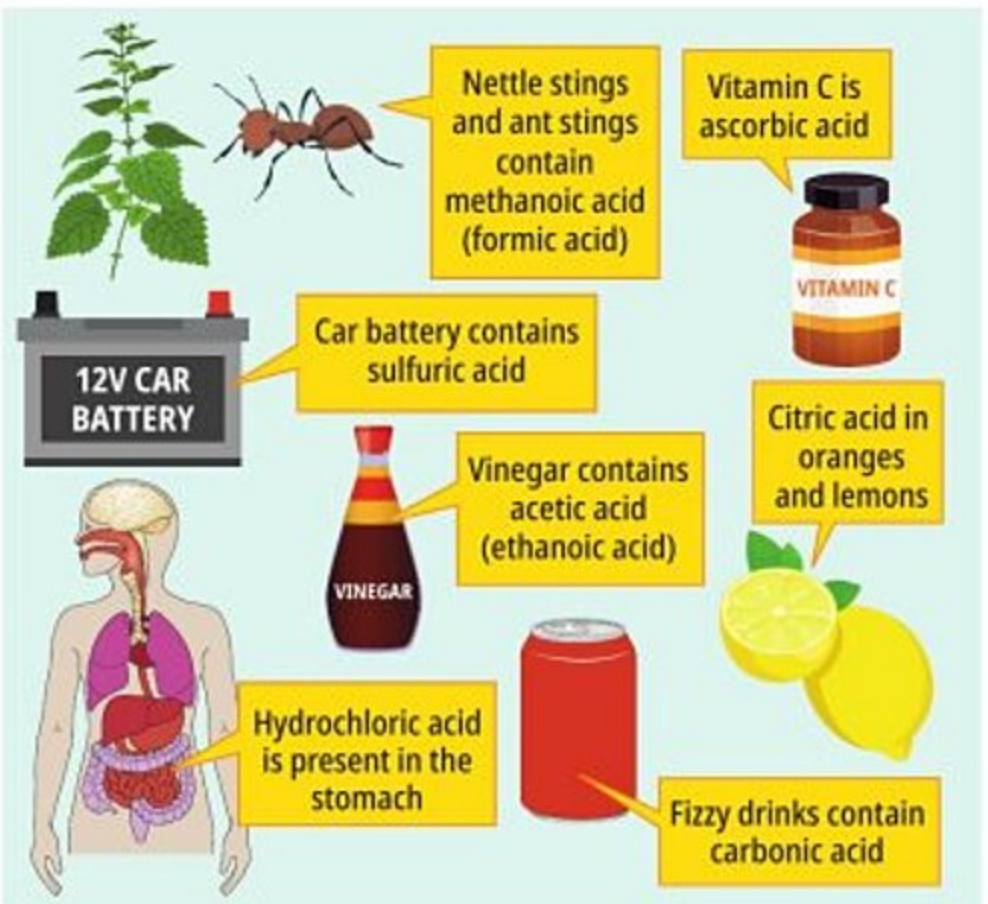

Nettle stings and ant stings contain methanoic acid (formic acid)
Vitamin C is ascorbic acid
VITAMIN C
12V CAR BATTERY
Car battery contains sulfuric acid
Vinegar contains acetic acid (ethanoic acid)
VINEGAR
Citric acid in oranges and lemons
Hydrochloric acid is present in the stomach
Fizzy drinks contain carbonic acid

Figure 11.1 Examples of everyday substances that contain acids

WINDOW CLEANER
OVEN CLEANER
Window cleaner and over cleaner contain ammonia solution
Toothpaste contains bases such as calcium carbonate
Bath salts contain the base sodium carbonate
Milk of Magnesia
Drain cleaner contains a base called sodium hydroxide (caustic soda)
Milk of Magnesia and indigestion tablets contain the base magnesium hydroxide
Caustic Soda
Baking powder contains the base sodium hydrogencarbonate

Figure 11.2 Examples of everyday substances containing bases

- Bases that dissolve in water are called **alkalis**. Sodium hydroxide (caustic soda), NaOH, is an example of an alkali. It dissolves in water and is very corrosive – especially to skin!
- You may have some caustic soda at home as it is used to clear blocked drains. It works by breaking down the material blocking the drain. Always wear safety glasses and gloves when handling sodium hydroxide as it is highly corrosive.
- Bases are often used in products that remove grease. This is because they react with fats to form soap.
- Many household cleaners (e.g. oven cleaners and window cleaners) contain soluble bases to help remove grease. They convert oil and grease into soluble soaps, which are easily washed away.
- Another example of a base is magnesium hydroxide, $Mg(OH)_2$, found in *Milk of Magnesia* and *Maalox*.
- Calcium hydroxide, $Ca(OH)_2$, commonly called lime or slaked lime, produces 'limewater' when dissolved in water; limewater is used to detect the presence of carbon dioxide.

Figure 11.3 (a) Acids turn blue litmus paper red. (b) Bases turn red litmus paper blue.

We will be studying the reactions of acids and bases in more detail in this chapter and subsequent chapters. However, let us now go to Sweden where the first major attempt was made to accurately define the terms *acid* and *base*.

11.2 Arrhenius theory of acids and bases

In 1884 a young Swedish student called Svante Arrhenius submitted his PhD thesis at the University of Uppsala, Sweden, Figure 11.4. In his thesis, he put forward a theory that acid and bases when added to water dissociate (break up) into ions. Unfortunately, the examiners of his thesis were not impressed by his work, and he was awarded the lowest possible grade to pass the exam!

However, Arrhenius was not discouraged and moved to Stockholm University where his outstanding work was recognised. In 1903 he was awarded the Nobel Prize in chemistry for the thesis that was awarded such a low grade by his examiners. So if you ever feel disappointed that your chemistry teacher does not recognise that you are a genius, just think of Arrhenius!

Figure 11.4 The Swedish chemist Arrhenius put forward one of the first definitions of acids and bases.

Arrhenius defined an acid as follows:

> Arrhenius definition: An **acid** is a substance that dissociates in water to produce H^+ ions.

For example, when hydrogen chloride is added to water, it dissociates, or breaks up, into H^+ ions and Cl^- ions:

$$HCl \rightarrow H^+ + Cl^-$$

Similarly, the dissociation of nitric acid and sulfuric acid may be represented as:

$$HNO_3 \rightarrow H^+ + NO_3^-$$

$$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$$

- A solution of hydrogen chloride gas in water is commonly called hydrochloric acid. Acids such as hydrochloric acid and nitric acid, molecules of which dissociate to give **one** H^+ ion in aqueous solution, are called **monobasic** (or monoprotic) acids.

  Monobasic: $HCl \rightarrow H^+ + Cl^-$

- Acids such as sulfuric acid, a molecule of which can dissociate to give **two** H^+ ions in aqueous solution are called **dibasic** (or diprotic) acids.

  Dibasic: $H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

- An acid such as phosphoric acid, H_3PO_4, a molecule of which can dissociate to give **three** H^+ ions in aqueous solution, is called a **tribasic** (or triprotic) acid.

  Tribasic: $H_3PO_4 \rightarrow 3H^+ + PO_4^{3-}$

Acids such as hydrochloric acid, sulfuric acid and nitric acid are described as **strong acids** since they fully dissociate in water, i.e. almost every molecule breaks up to give H^+ ions.

Arrhenius definition: A **strong acid** is a substance that almost completely dissociates in water to give hydrogen ions.

On the contrary, acids such as ethanoic acid (acetic acid) and methanoic acid (formic acid) are described as **weak acids** since they dissociate only to a slight extent in water.

Arrhenius definition: A **weak acid** is a substance that only slightly dissociates in water to give hydrogen ions.

- As knowledge about atomic structure developed, chemists realised that a H^+ ion (a hydrogen atom that had lost an electron) is simply a bare proton.
- Arrhenius did not realise that it was not possible for a bare proton to exist independently in solution.
- In fact, it was discovered that the H^+ ion actually reacts with a water molecule to form the H_3O^+ ion. The formation of this ion is shown in Figure 11.5.

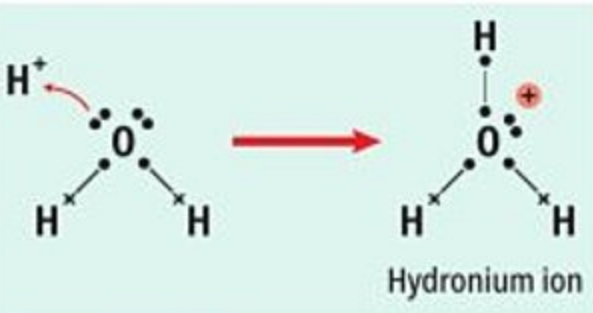


Figure 11.5 The H^+ ion reacts with a water molecule to form the H_3O^+ ion, which is called the hydronium ion (or oxonium ion).

Note in this diagram that one of the lone pairs on the oxygen atom forms a covalent bond with the proton. Both electrons in this bond come from the same atom (the oxygen atom). Such a bond is often called a **dative** covalent bond or a **coordinate** covalent bond. (The word 'dative' is a Latin word meaning 'giving' since the same atom gives both of the shared pair of electrons in the bond.)

The H_3O^+ ion is called the 'hydronium ion', the 'hydroxonium ion' and occasionally the 'oxonium ion'. In this textbook we use the term ***hydronium ion***, since this term is the most widely used. The hydronium ion is a very common ion – it is present in every acidic solution.

Since aqueous solutions of acids contain H_3O^+ ions – and not H^+ ions – it is more accurate to represent the dissociation of acids in water as:

$$HA + H_2O \rightarrow H_3O^+ + A^-$$
$$\text{e.g. } HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

For the sake of simplicity, many chemists use the term *hydrogen ion* when talking about acidic solutions – even though hydrogen ions do not exist in solution. The above equation recognises the essential role of the water molecules in the dissociation of acids. If substances such as pure ethanoic acid (acetic acid) or pure hydrogen chloride are added to solvents such as benzene or methylbenzene, no H^+ or H_3O^+ ions are found to be present. A piece of dry blue litmus paper added to these solutions does not show any colour change. Thus, substances such as ethanoic acid and hydrogen chloride only show acidic properties when dissolved in water.

EXAM TIP!

If 'hydrogen chloride' or 'HCl' is required as an answer in an exam, 'hydrochloric acid' will not be accepted as a correct answer. So read the question carefully!

In his study of bases, Arrhenius proposed the idea that bases dissociate into ions when added to water. He defined a base as follows:

Arrhenius definition: A **base** is a substance that dissociates in water to produce OH^- ions.

The OH^- ion is commonly called the hydroxide ion. For example, when sodium hydroxide is added to water, it dissociates or breaks up into Na^+ ions and OH^- ions:

$$NaOH \rightarrow Na^+ + OH^-$$

Similarly, the dissociation of magnesium hydroxide and calcium hydroxide may be represented as:

$$Mg(OH)_2 \rightarrow Mg^{2+} + 2OH^-$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$$

Since sodium hydroxide dissociates almost completely in water to give OH^- ions, it is referred to as a **strong base**, Figure 11.6.

Figure 11.6 Sodium hydroxide, NaOH, and calcium hydroxide, $Ca(OH)_2$, are strong bases. However, magnesium hydroxide, $Mg(OH)_2$, and aluminium hydroxide $Al(OH)_3$, are weak bases.

Arrhenius definition: A **strong base** is a substance that almost completely dissociates in water to give hydroxide (hydroxyl) ions.

The solubility of calcium hydroxide in water is low. However, the dissolved portion dissociates completely. Therefore, calcium hydroxide is classified as a strong base. On the other hand, magnesium hydroxide, $Mg(OH)_2$ and aluminium hydroxide, $Al(OH)_3$, dissociate only to a slight extent in water and hence are referred to as **weak bases**.

Arrhenius definition: A **weak base** is a substance that only slightly dissociates in water to give hydroxide ions.

Shortcomings of the Arrhenius theory

Although the theory of acids and bases put forward by Arrhenius is a reasonably adequate one, it does have a number of shortcomings:

1. **Hydronium ions.** As already stated, it is hydronium ions, H_3O^+, rather than the bare H^+ ions suggested by Arrhenius, that exist in solution.
2. **Aqueous solutions.** Arrhenius restricted his definitions to aqueous solutions, i.e. reactions occurring in water. Solvents such as liquid ammonia, benzene and methylbenzene (toluene) are excluded from his definitions.
3. **Dissolving in water.** Not all acid–base reactions require water. For example, in Chapter 2 we learned that, when ammonia gas and hydrogen chloride gas come in contact with each other, white fumes of ammonium chloride are formed, Figure 11.7.

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{HCl} \rightarrow \underset{\text{ammonium chloride}}{NH_4Cl}$$

Figure 11.7 The reaction between HCl gas and NH_3 gas to form white fumes of NH_4Cl is an acid–base reaction. However, since water is not involved, this would not be classified as an acid–base reaction using the Arrhenius theory

However, the Arrhenius definitions of acids and bases would not allow us to classify the above reaction as an acid–base reaction, since there is no water present.

In view of the limitations of the Arrhenius definitions, we now consider a more modern theory of acids and bases.

11.3 Brønsted–Lowry theory of acids and bases

In 1923 Johannes Brønsted, a Danish chemist, and Thomas Lowry, an English chemist, independently of each other proposed new definitions of an acid and of a base, Figure 11.8.

Figure 11.8 Johannes Brønsted (right) and Thomas Lowry independently developed the Brønsted–Lowry theory of acids and bases.

Since the properties of acids and bases were, in many respects, opposed to each other, they believed it would make more sense to have definitions that were opposed to each other. These definitions are:

Brønsted–Lowry definition:
An **acid** is a proton donor.

Brønsted–Lowry definition:
A **base** is a proton acceptor.

Let us now consider these definitions in a little more detail. When hydrogen chloride is added to water, we have already learned that the following reaction occurs:

$$\underset{\substack{\text{donates}\\ \text{a proton}\\ \therefore \text{ B/L acid}}}{HCl} + \underset{\substack{\text{accepts}\\ \text{a proton}\\ \therefore \text{ B/L base}}}{H_2O} \rightarrow H_3O^+ + Cl^-$$

In this reaction we see that a molecule of HCl donates a proton to a molecule of water. Since HCl is a proton donor, it is classified as an **acid**. Since the molecule of water accepts a proton, it is classified as a **base**.

Consider what happens when ammonia gas is dissolved in water:

$$\underset{\text{accepts a proton}\\ \therefore \text{B/L base}}{NH_3} + \underset{\text{donates a proton}\\ \therefore \text{B/L acid}}{H_2O} \rightarrow NH_4^+ + OH^-$$

Since the ammonia molecule accepts a H^+ ion from a water molecule, the ammonia molecule is acting as a base and the water molecule is acting as an acid. This reaction is shown in Figure 11.9.

The strengths of acids and bases are easily described in terms of the Brønsted–Lowry theory as follows:

Brønsted–Lowry definitions:

- A **strong acid** is a good proton donor.
- A **weak acid** is a poor proton donor.
- A **strong base** is a good proton acceptor.
- A **weak base** is a poor proton acceptor.

- It is clear, from the above examples of HCl reacting with water and also of NH_3 reacting with water, that water can act as either an acid or a base.
- A substance that can act either as an acid or a base is said to be **amphoteric** or **amphiprotic**.
- The word 'amphi' comes from the Greek meaning 'on both sides'. The word 'amphibian' (an animal such as a frog, which lives on both land and in water) may help you to remember this term.
- The word 'protic' refers to protons.
- Therefore, an amphiprotic substance is one that can donate or accept protons.

The Brønsted–Lowry theory of acids and bases may be applied to acid–base reactions that do not involve water as the solvent.

- An example would be the reaction between HCl gas and NH_3 gas as shown in Figure 11.7.

$$\underset{\text{donates a proton}\\ \therefore \text{B/L acid}}{HCl} + \underset{\text{accepts a proton}\\ \therefore \text{B/L base}}{NH_3} \rightarrow NH_4^+ + Cl^-$$

- Note that in the above equations, an acid will only donate a proton if there is something else present to accept this proton.
- Similarly, a base can only accept a proton if there is something else present to donate the proton.

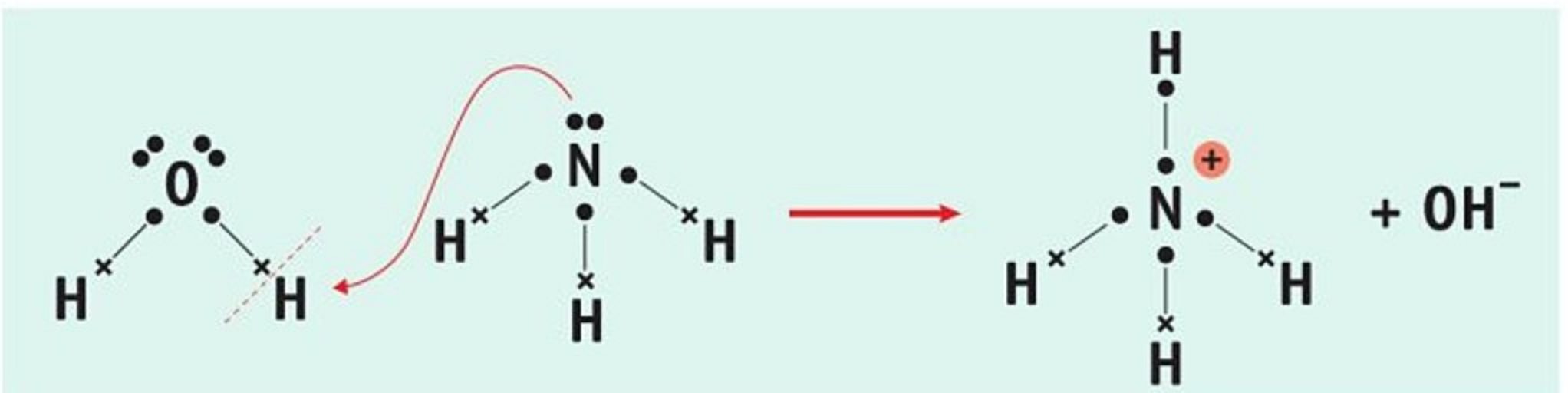


Figure 11.9 The water molecule donates a proton to the ammonia molecule. Thus, the water molecule is acting as an acid and the ammonia molecule is acting as a base.

Comparing the Arrhenius theory and the Brønsted–Lowry theory

1. The Arrhenius theory is limited to reactions in water (aqueous solutions). The Brønsted–Lowry theory is more general and not limited to reactions in water but also applies to reactions in the gaseous state and in solvents other than water. For example, in the above reaction between HCl and NH_3 in liquid ammonia or in the gaseous state, the hydrogen chloride molecule acts as an acid by donating a proton to the ammonia molecule. No water molecules are present.

2. The Arrhenius theory is limited to bases that produce hydroxide ions in water but not all bases produce hydroxide ions, e.g. there are no oxygen atoms in NH_3 so it is impossible for NH_3 to produce OH^- ions.

3. Substances that would not be classified as acids or bases in the Arrhenius theory are classified as acids or bases in the Brønsted–Lowry theory, i.e. the Brønsted–Lowry definitions broaden the range of species that can be defined as acids and bases. For example, in reactions, both carbonate (CO_3^{2-}) and hydrogencarbonate ions (HCO_3^-) can accept H^+ ions. Therefore, they are classified as bases by the Brønsted–Lowry theory but not by the Arrhenius theory.

4. The Arrhenius theory does not take the existence of hydronium ions into account but the Brønsted–Lowry theory does.

5. The Arrhenius theory cannot explain how a substance can act as both an acid and a base (i.e. an amphoteric substance) but the Brønsted–Lowry theory explains this in terms of proton transfer.

These points are summarised in Table 11.1.

Feature	Arrhenius theory	Brønsted–Lowry theory
1. Role of water	Limited to reactions in water.	Not limited to reactions in water. Can apply to reactions between gases and in solvents other than in water.
2. Hydroxide ions	Limited to substances that produce hydroxide (OH^-) ions.	Applies to any substance that can accept a proton, e.g. the NH_3 molecule does not produce OH^- ions.
3. Classification as acids or bases	Only substances with OH^- ions are classified as bases. Therefore, substances such as carbonate ions and hydrogencarbonate ions are not classified as bases by the Arrhenius theory.	Has a more general classification. Since carbonate and hydrogencarbonate ions can accept protons, these are classified as bases by the Brønsted–Lowry theory.
4. Hydronium ion	Does not take the existence of hydronium ion into account.	Explains the existence of the hydronium ion.
5. Amphoteric substances	Does not explain how a substance can act as both an acid and a base.	Explains amphoteric substances in terms of proton loss and proton gain.

Table 11.1 Comparing the Arrhenius Theory and Brønsted–Lowry theory of acids and bases

In short, the two theories are not in conflict with each other. The Brønsted–Lowry theory adds to the Arrhenius theory and improves our understanding of reactions involving acids and bases.

TEST YOURSELF: Attempt Questions 11.1 and W11.1.

11.4 Conjugate acid–base pairs

Ethanoic acid (acetic acid), CH_3COOH, is the acid found in vinegar. When pure ethanoic acid is added to water, the following reaction occurs:

$$CH_3COOH + H_2O \rightarrow CH_3COO^- + H_3O^+$$

It is found that this reaction also takes place in the reverse direction, i.e. the following reaction also takes place:

$$CH_3COO^- + H_3O^+ \rightarrow CH_3COOH + H_2O$$

We use the symbol like $\rightleftharpoons$ to indicate that a reaction takes place in both directions:

$$\underset{\substack{\text{donates}\\\text{a proton}\\\therefore \text{B/L acid}}}{CH_3COOH} + \underset{\substack{\text{accepts}\\\text{a proton}\\\therefore \text{B/L base}}}{H_2O} \rightleftharpoons CH_3COO^- + H_3O^+$$

Consider the reaction in the forward direction. In this reaction, the CH_3COOH molecule donates a proton to the H_2O molecule, i.e. the CH_3COOH molecule is behaving as an acid and the H_2O molecule is behaving as a base. In the reverse direction, the CH_3COO^- ion accepts a proton from the H_3O^+ ion, i.e. the CH_3COO^- ion is behaving as a base and the H_3O^+ ion is behaving as an acid.

$$\underset{\substack{\text{accepts}\\\text{a proton}\\\therefore \text{B/L base}}}{CH_3COOH + H_2O} \rightleftharpoons \underset{\substack{\text{donates}\\\text{a proton}\\\therefore \text{B/L acid}}}{CH_3COO^- + H_3O^+}$$

Note from the above equations that CH_3COOH changes into CH_3COO^- by donating a proton. Also, CH_3COO^- changes into CH_3COOH by accepting a proton. We say that CH_3COO^- is the **conjugate base** of CH_3COOH.

An acid changes into its **conjugate base** when it donates a proton.

$$\underset{\text{acid}}{CH_3COOH} \rightarrow \underset{\text{conjugate base}}{CH_3COO^-} + \underset{\text{proton}}{H^+}$$

CH_3COOH is said to be the **conjugate acid** of CH_3COO^-.

A base changes into its **conjugate acid** when it accepts a proton.

$$\underset{\text{base}}{CH_3COO^-} + H^+ \rightarrow \underset{\text{conjugate acid}}{CH_3COOH}$$

Every acid has a conjugate base and every base has a conjugate acid.

Since CH_3COOH and CH_3COO^- only differ by a proton, we refer to this pair as a **conjugate acid–base pair** or simply a **conjugate pair**.

$$\underset{\text{acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{base}}{CH_3COO^-} + \underset{\text{acid}}{H_3O^+}$$

conjugate acid–base pair

conjugate acid–base pair

Similarly, H_2O and H_3O^+ are a conjugate acid–base pair, since they differ only by one proton.

A **conjugate acid–base pair (conjugate pair)** is any pair consisting of an acid and a base that differ by one proton.

Note from the definition that there is only a single (one) proton difference between the conjugate acid–base pair. Sometimes chemists use the formula HA to represent an acid. Its conjugate base is represented as A^- and the equation relating them is then written as follows:

$$HA \rightleftharpoons A^- + H^+$$

EXAM TIP!

Since the definitions of a conjugate acid, conjugate base and conjugate acid–base pair all specify a single proton, it follows that the conjugate base of H_2SO_4 is HSO_4^- and not SO_4^{2-}.

Example 11.1

Question

What is **(i)** the conjugate acid, **(ii)** the conjugate base of $HC_2O_4^-$? [LCH]

Answer

(i) A base changes into its conjugate acid by accepting a proton. Therefore, if $HC_2O_4^-$ is to change into its conjugate acid it must accept a proton, i.e. the following reaction must occur:

$$\underset{\text{base}}{HC_2O_4^-} + H^+ \rightarrow \underset{\text{conjugate acid}}{H_2C_2O_4}$$

Therefore, **the conjugate acid is $H_2C_2O_4$.**

(ii) An acid changes into its conjugate base by donating a proton. Therefore, if $HC_2O_4^-$ is to change into its conjugate base it must donate a proton, i.e. the following reaction must occur:

$$\underset{\text{acid}}{HC_2O_4^-} \rightarrow H^+ + \underset{\text{conjugate base}}{C_2O_4^{2-}}$$

Therefore, **the conjugate base is $C_2O_4^{2-}$.**

Example 11.2

Question

Indicate which species are acting as acids and which are acting as bases:

$HNO_3 + H_2F_2 \rightarrow H_2NO_3^+ + HF_2^-$ Also indicate the conjugate acid–base pairs.

Answer

Working from left to right, we see that HNO_3 accepts a proton from H_2F_2 i.e. HNO_3 is acting as a base. The HNO_3 changes into $H_2NO_3^+$ (the conjugate acid). H_2F_2 is acting as an acid since it donates a proton to HNO_3.

Working from right to left, we see that $H_2NO_3^+$ donates a proton to HF_2^-. Therefore, $H_2NO_3^+$ is acting as an acid and HF_2^- is acting as a base.

We indicate the conjugate acid–base pairs by linking up the species that differ by a proton.

$$\underset{\text{base}}{HNO_3} + \underset{\text{acid}}{H_2F_2} \rightleftharpoons \underset{\text{acid}}{H_2NO_3^+} + \underset{\text{base}}{HF_2^-}$$

conjugate acid–base pair

conjugate acid–base pair

EXAM TIP!

In an exam, it is very important that you clearly indicate the pairing as shown.

Example 11.3

Question

Explain, by giving a balanced equation for its dissociation in water, that the conjugate base of sulfuric acid is itself an acid. [LCH]

Answer

The conjugate base of sulfuric acid is HSO_4^-.

The balanced equation for its dissociation in water is:

$HSO_4^- + H_2O \rightarrow SO_4^{2-} + H_3O^+$

The HSO_4^- ion donates a proton to the water molecule, i.e. HSO_4^- is acting as an acid.

TEST YOURSELF: Attempt Questions 11.2–11.7 and W11.2–W11.5.

11.5 Types of reactions involving acids and bases

There are three types of reactions involving acids and bases on your course:

1. Acid-base neutralisation
2. Reactions between acids and carbonates
3. Reactions between acids and metals.

EXAM TIP!

For your exam, you need to be able to predict the products of acid–base reactions and also write balanced chemical equations for these reactions.

11.5.1 Neutralisation

When acids and bases react with each other in the right proportions, it is found that they 'cancel' each other out and both the acid and the base lose their characteristic properties. Since the solution formed has no effect on litmus (i.e. the solution is neutral), the process is called **neutralisation**.

Consider the reaction between hydrochloric acid and sodium hydroxide, Figure 11.10.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

Figure 11.10 The reaction between an acid and a base produces a salt.

A **salt** is the substance formed when the hydrogen ion from an acid is replaced by a metal or by an ammonium ion.

Note that the reaction between the acid and the base produces a salt – in this case, sodium chloride or common table salt. The word 'salt' is a general term and is defined as follows:

Thus, when the hydrogen ion from hydrochloric acid HCl is replaced by a sodium ion, the salt sodium chloride, NaCl is formed. When the H^+ ion in $HCl_{(aq)}$ is replaced by NH_4^+, the salt ammonium chloride, NH_4Cl, is formed. [$HCl_{(aq)}$ is hydrochloric acid]

Neutralisation is the reaction between an acid and a base to form a salt and water.

The process of neutralisation may be defined as:

It is worth remembering the following, if you are ever asked to write a chemical equation for a neutralisation reaction.

Acid + Base → Salt + Water

In order to understand what is happening in a neutralisation reaction, consider the ions that are present in solution.

$$HCl + NaOH \rightarrow NaCl + H_2O$$

i.e. in solution: $H^+ + \cancel{Cl^-} + \cancel{Na^+} + OH^- \rightarrow \cancel{Na^+} + \cancel{Cl^-} + H_2O$

If we ignore the ions that are present on both sides of the equation ('spectator ions'), the above equation becomes:

$$H^+ + OH^- \rightarrow H_2O$$

Thus, neutralisation occurs because the hydrogen ions (or more precisely the hydronium ions) from the acid react with the hydroxide ions from the base to form water. Some examples of neutralisation reactions are given in Table 11.2.

	acid	+	base	→	salt	+	water
1.	H_2SO_4 sulfuric acid	+	2NaOH sodium hydroxide	→	Na_2SO_4 sodium sulfate	+	$2H_2O$ water
2.	HCl hydrochloric acid	+	KOH potassium hydroxide	→	KCl potassium chloride	+	H_2O water
3.	2HCl hydrochloric acid	+	$Mg(OH)_2$ magnesium hydroxide	→	$MgCl_2$ magnesium chloride	+	$2H_2O$ water
4.	H_2SO_4 sulfuric acid	+	$Ca(OH)_2$ calcium hydroxide	→	$CaSO_4$ calcium sulfate	+	$2H_2O$ water
5.	HNO_3 nitric acid	+	NaOH sodium hydroxide	→	$NaNO_3$ sodium nitrate	+	H_2O water
6.	H_3PO_4 phosphoric acid	+	3KOH potassium hydroxide	→	K_3PO_4 potassium phosphate	+	$3H_2O$ water

Table 11.2 Some examples of balanced chemical equations for the reaction of acids and bases

Examples of neutralisation in our everyday lives

1. **Medicine.** Hydrochloric acid is produced by the stomach to help digest food. Sometimes the stomach produces too much HCl as a result of for example overeating or stress. If this condition persists, the lining of the stomach may be damaged and this may give rise to ulcers. Relief from excess HCl may be obtained by taking an antacid preparation that contains a base to neutralise the excess HCl, Figure 11.11.

Figure 11.11 Some indigestion remedies that are used to neutralise excess acid in the stomach

For example, *Alka-Seltzer* and *Bisodol* contain sodium hydrogencarbonate, which reduces the acidity in the stomach by the following neutralisation reaction:

HCl	+	$NaHCO_3$	→	NaCl	+	H_2O	+	CO_2
hydrochloric acid	+	sodium hydrogencarbonate	→	sodium chloride	+	water	+	carbon dioxide

Similarly, Milk of Magnesia, and Maalox contain magnesium hydroxide, which reacts with the hydrochloric acid as follows:

2HCl	+	$Mg(OH)_2$	→	$MgCl_2$	+	$2H_2O$
hydrochloric acid	+	magnesium hydroxide	→	magnesium chloride	+	water

2. **Agriculture.** If soil is too acidic, the yield of crops tends to be low, e.g. wheat and barley grow best in soils which are approximately neutral or slightly basic. Therefore, farmers often spread lime on soil to neutralise the acidity in the soil, Figure 11.12. Lime is calcium oxide, CaO, also known as quicklime. The calcium oxide reacts with water to form calcium hydroxide, $Ca(OH)_2$, commonly called slaked lime. (Ground limestone (calcium carbonate, $CaCO_3$), may also be used.)

Figure 11.12 Lime had been spread on these fields to neutralise the acidity in the soil.

CaO	+	H_2O	→	$Ca(OH)_2$
calcium oxide		water		calcium hydroxide

Calcium hydroxide neutralises the acidity in the soil as follows:

H_2SO_4	+	$Ca(OH)_2$	→	$CaSO_4$	+	$2H_2O$
sulfuric acid		calcium hydroxide		calcium sulfate		water

3. **Environmental protection.** In areas that suffer from acid rain, limestone is often added to lakes to neutralise the acidity.

H_2SO_4	+	$CaCO_3$	→	$CaSO_4$	+	H_2O	+	CO_2
sulfuric acid		limestone		calcium sulfate		water		carbon dioxide

Limestone is often used in the tall chimneys of coal-burning power plants. The limestone neutralises the acidic substances formed as a result of burning coal.

4. **Miscellaneous.** Toothpaste is slightly basic to neutralise the acids in the foods that cause tooth decay. Baking soda (sodium hydrogencarbonate) is used to neutralise the acidic sting of bees. Vinegar is used to neutralise the alkaline sting of wasps. Shampoo is slightly basic and this can cause the scales that coat the surface of each hair to open out. Hair conditioner is slightly acidic to neutralise the base in shampoo. This causes the scales on each hair to close down and leaves the hair more manageable and shiny, Figure 11.13.

Figure 11.13 The reaction between hair conditioner and shampoo is an example of a neutralisation reaction.

11.5.2 Reactions between acids and carbonates

In the previous section, we studied neutralisation reactions. You will have noticed that in some cases, we took the reaction between acids and carbonates as examples of neutralisation reactions. Carbonates are good examples of bases because the carbonate ion is a proton acceptor. The general reaction between an acid and carbonate may be summarised as follows:

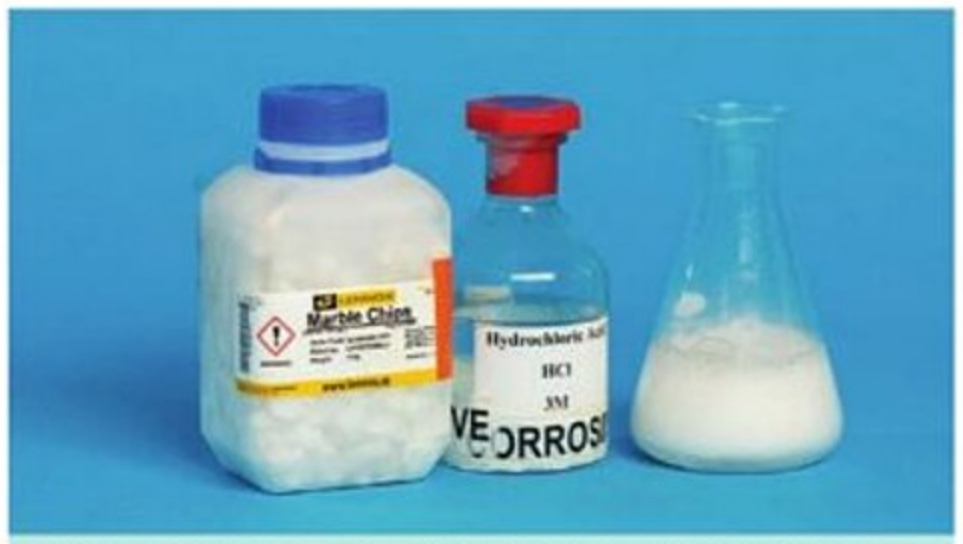


Figure 11.14 The reaction between hydrochloric acid and marble chips forms calcium chloride, water and carbon dioxide. Note the bubbles of carbon dioxide being produced.

Acid + Carbonate → Salt + Water + Carbon Dioxide

One of the best-known examples of this type of reaction is used in the preparation of carbon dioxide gas. Note the fizzing that takes place when hydrochloric acid is added to calcium carbonate (also called limestone or marble).

Figure 11.15 This limestone statue has been worn away by the reaction between acid rain and calcium carbonate.

$$\underset{\text{hydrochloric acid}}{2HCl} + \underset{\text{calcium carbonate}}{CaCO_3} \rightarrow \underset{\text{calcium chloride}}{CaCl_2} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

Note the bubbles of carbon dioxide formed in the above reaction, Figure 11.14.

The above reaction is responsible for the damage caused to limestone buildings and statues by acid rain, Figure 11.15.

Some further examples of acid–carbonate reactions are given in Table 11.3. You don't have to learn these off, but note the reaction that is common to all of them.

	acid	+	base	→	salt	+	water	+	carbon dioxide
1.	H_2SO_4 sulfuric acid	+	$CaCO_3$ calcium carbonate	→	$CaSO_4$ calcium sulfate	+	H_2O water	+	CO_2 carbon dioxide
2.	$2HCl$ hydrochloric acid	+	$MgCO_3$ magnesium carbonate	→	$MgCl_2$ magnesium chloride	+	H_2O water	+	CO_2 carbon dioxide
3.	$2HCl$ hydrochloric acid	+	Na_2CO_3 sodium carbonate	→	$2NaCl$ sodium chloride	+	H_2O water	+	CO_2 carbon dioxide
4.	H_2SO_4 sulfuric acid	+	Na_2CO_3 sodium carbonate	→	Na_2SO_4 sodium sulfate	+	H_2O water	+	CO_2 carbon dioxide
5.	$2HNO_3$ nitric acid	+	Na_2CO_3 sodium carbonate	→	$2NaNO_3$ sodium nitrate	+	H_2O water	+	CO_2 carbon dioxide
6.	$2HNO_3$ nitric acid	+	$MgCO_3$ magnesium carbonate	→	$Mg(NO_3)_2$ magnesium nitrate	+	H_2O water	+	CO_2 carbon dioxide
7	H_2SO_4 sulfuric acid	+	$BaCO_3$ barium carbonate	→	$BaSO_4$ barium sulfate	+	H_2O water	+	CO_2 carbon dioxide
8.	$2H_3PO_4$ phosphoric acid	+	$3Na_2CO_3$ sodium carbonate	→	$2Na_3PO_4$ sodium phosphate	+	$3H_2O$ water	+	CO_2 carbon dioxide

Table 11.3 Some examples of balanced chemical equations for the reaction of acids and carbonates

11.5.3 Reactions between acids and metals

You may recall from Junior Cycle chemistry that metals such as magnesium and zinc reacted with acids to produce hydrogen gas. The reaction between magnesium and hydrochloric acid is often used to investigate the factors that affected the rate of the following reaction:

$2HCl$	+	Mg	→	$MgCl_2$	+	H_2
hydrochloric acid		magnesium		magnesium chloride		hydrogen

Magnesium chloride is an example of a salt. Recall that a salt is the substance formed when the hydrogen ion from an acid is replaced by a metal or an ammonium ion. The 'H^+' in a solution of HCl has been replaced by 'Mg^{2+}' to form the salt magnesium chloride.

Many metals react with acids to form a salt and hydrogen gas.

Acid + Metal → Salt + Hydrogen gas

Some more examples of acid–metal reactions are given in Table 11.4. You don't have to learn these off but note the reaction that is common to all of them.

	acid	+	base	→	salt	+	hydrogen gas
1.	H_2SO_4 sulfuric acid	+	Mg magnesium	→	$MgSO_4$ magnesium sulfate	+	H_2 hydrogen
2.	$2HCl$ hydrochloric acid	+	Zn zinc	→	$ZnCl_2$ zinc chloride	+	H_2 hydrogen
3.	$6HCl$ hydrochloric acid	+	$2Al$ aluminium	→	$2AlCl_3$ aluminium chloride	+	$3H_2$ hydrogen
4.	H_2SO_4 sulfuric acid	+	Zn zinc	→	$ZnSO_4$ zinc sulfate	+	H_2 hydrogen
5.	$2HNO_3$ nitric acid	+	Mg magnesium	→	$Mg(NO_3)_2$ magnesium nitrate	+	H_2 hydrogen
6.	H_2SO_4 sulfuric acid	+	Fe iron	→	$FeSO_4$ iron sulfate	+	H_2 hydrogen

Table 11.4 Some examples of balanced chemical equations for the reaction of acids and metals.

The reaction of acids with metals can cause problems in our everyday lives. For example, acid rain can cause steel structures to corrode, Figure 11.16, as iron reacts with the sulfuric acid in acid rain to form iron sulfate as shown in the above equation.

Not all metals react with dilute solutions of acids. For example, metals such as silver, gold and platinum are very unreactive and do not react with acids.

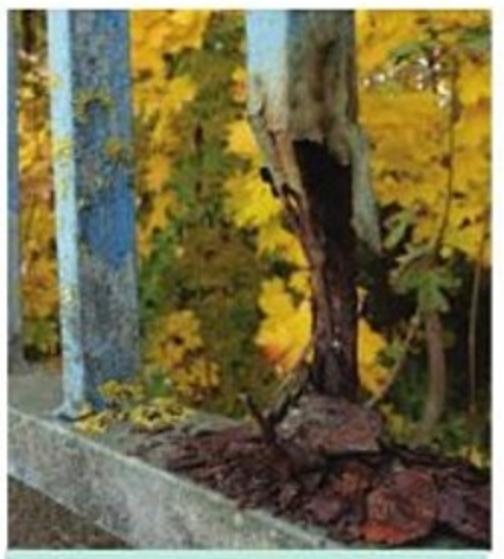


Figure 11.16 The reaction of acids with metals can cause corrosion.

TEST YOURSELF: Attempt Questions 11.8–11.9 and W11.6–W11.15.

Highly reactive metals such as sodium and potassium should never be added to acids, as so much hydrogen is given off so quickly that there is a violent explosion.

Summary What I should know

- There are many everyday substances that contain acids or bases.
- The Arrhenius definition of an acid is that it is a substance that dissociates in water to produce H^+ ions.
- The Arrhenius definition of a base is that it is a substance that dissociates in water to produce OH^- ions.
- Arrhenius definitions: A strong acid is a substance that almost completely dissociates in water to give hydrogen ions. A weak acid is a substance that only slightly dissociates in water to give hydrogen ions. A strong base is a substance that almost completely dissociates in water to give hydroxide ions. A weak base is a substance that only slightly dissociates in water to give hydroxide ions.
- The Brønsted–Lowry definition of an acid is that an acid is a proton donor.
- The Brønsted–Lowry definition of a base is that a base is a proton acceptor.
- Brønsted–Lowry definitions: A strong acid is a good proton donor. A weak acid is a poor proton donor. A strong base is a good proton acceptor. A weak base is a poor proton acceptor.
- A substance that can act both as an acid and as a base is said to be amphoteric or amphiprotic.
- An acid changes into its conjugate base when it donates a proton.
- A base changes into its conjugate acid when it accepts a proton.
- A conjugate acid–base pair (conjugate pair) is defined as any pair consisting of an acid and a base that differ by one proton.
- Neutralisation is the reaction between an acid and a base to form a salt and water.
- Acid + Carbonate → Salt + Water + Carbon Dioxide
- Acid + Metal → Salt + Hydrogen gas

Learning outcomes

At the end of this chapter, I should be able to:			
Identify examples of acids and bases in our everyday lives.	⬡	⬡	⬡
Explain the Arrhenius theory and Brønsted–Lowry theory of acids and bases.	⬡	⬡	⬡
Compare and justify why the Brønsted–Lowry theory is a more extensive model than the Arrhenius theory.	⬡	⬡	⬡
Predict the products and write balanced equations for acid–base neutralisation reactions, acid–metal reactions and acid–carbonate reactions.	⬡	⬡	⬡

Chapter review questions

11.1 **(a)** Give two examples of acids that are commonly found in food.

(b) How do acids and bases differ with regard to their effect on litmus?

(c) What name is given to a solution of hydrogen chloride in water?

(d) Explain why bases tend to have a soapy feel.

(e) Write down the Arrhenius definition of an acid.

(f) Write an equation to show how the HSO_4^- ion can act as an Arrhenius acid.

(g) Write an equation to show how the HSO_4^- ion can act as a Brønsted–Lowry base.

(h) Define an acid in terms of the Brønsted–Lowry theory. [LCH]

(i) What is the formula for the hydronium ion?

(j) Distinguish between a strong acid as defined by the Arrhenius theory and a strong acid as defined by the Brønsted–Lowry theory.

(k) Name the acid found in car batteries.

(l) How did Brønsted and Lowry define a base?

(m) Give one advantage of the Brønsted–Lowry theory compared to the Arrhenius theory. [LCH]

11.2 Write down the conjugate base of each of the following Brønsted–Lowry acids:

(a) HCl, **(b)** H_3O^+, **(c)** HSO_4^-, **(d)** $H_2PO_4^-$, **(e)** H_2S, **(f)** HSO_3^-, **(g)** $HClO_2$, **(h)** HNO_2.

11.3 Write down the conjugate acid of each of the following Brønsted–Lowry bases:

(a) CH_3COO^-, **(b)** $H_2PO_4^-$, **(c)** HPO_4^{2-}, **(d)** HSO_3^-, **(e)** H_2O, **(f)** CH_3NH^-, **(g)** SO_3^{2-}, **(h)** NH_2^-.

11.4 Identify the species acting as bases in the dissociation of nitrous acid in aqueous solution.

$HNO_2 + H_2O \rightleftharpoons H_3O^+ + NO_2^-$ [LCH]

11.5 Orthophosphoric acid, H_3PO_4, is a tribasic acid. The equation for the first dissociation of the acid in aqueous solution is

$H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$

Write an equation for the second dissociation in aqueous solution. Indicate the conjugate pairs present in the second dissociation. [LCH]

11.6 Write down each of the following equations and indicate in each case the acids, bases and conjugate acid–base pairs present.

(a) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

(b) $HSO_4^- + HNO_2 \rightleftharpoons H_2NO_2^+ + SO_4^{2-}$

(c) $H_2SO_4 + HF \rightleftharpoons H_2F^+ + HSO_4^-$ [LCH]

(d) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$

(e) $HSO_4^- + OH^- \rightleftharpoons SO_4^{2-} + H_2O$ [LCH]

(f) $CH_3COOH + HNO_3 \rightleftharpoons CH_3COOH_2^+ + NO_3^-$

(g) $O^{2-} + H_2O \rightleftharpoons OH^- + OH^-$

(h) $HOCl + OH^- \rightleftharpoons H_2O + ClO^-$

(i) $H^- + H_2O \rightleftharpoons OH^- + H_2$

(j) $HCN + H_2SO_4 \rightleftharpoons H_2CN^+ + HSO_4^-$

11.7 **(a)** Explain why ammonia (NH_3) is considered to be a base according to the Brønsted–Lowry theory, but is not considered to be a base according to the Arrhenius theory.

The self-ionisation of liquid ammonia is described by the following balanced chemical equation:

$NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(b) Identify the conjugate acid of NH_3 in this equilibrium.

(c) Identify the conjugate base of NH_3 in this equilibrium. [LCH]

11.8 **(a)** What is meant by the term *neutralisation* in chemistry?

(b) Explain the term *salt*.

(c) Write a balanced chemical equation for the reaction between hydrochloric acid and calcium hydroxide.

(d) Explain how an antacid containing sodium hydrogencarbonate works to reduce excess hydrochloric acid in the stomach. Your explanation should include a balanced chemical equation.

(e) What is lime (quicklime)? Why do farmers sometimes spread lime on soil?

11.9 Predict the products of the following chemical reactions and write a balanced chemical equation for each reaction in your copybook.

(a) $HNO_3 + KOH \rightarrow$

(b) $H_3PO_4 + NaOH \rightarrow$

(c) $H_2SO_4 + CaCO_3 \rightarrow$

12 Volumetric Analysis: Acid–Base

OBJECTIVES

- To give students an introduction to chemical solutions and concepts associated with chemical solutions.
- To make students familiar with the units for expressing concentrations of solutions.
- To provide students with the opportunity to determine the concentrations of substances being analysed in volumetric analysis.

12.1 Introduction

In Chapter 11, we studied how the composition of substances could be determined by careful weighing. We called this method of analysis **gravimetric analysis**. Gravimetric analysis is one of the branches of **quantitative analysis**, i.e. finding the quantities or amounts of materials present. (Do not confuse this with **qualitative analysis**, where we simply identify the presence of substances without finding the quantities present, e.g. testing for anions in Experiment 5.1 is an example of qualitative analysis.) The other main branch of quantitative analysis is **volumetric analysis**. As the name suggests, this method of analysis involves reacting volumes of solutions with each other.

Volumetric analysis has many applications not only in the school laboratory but also in industry and in research, Figure 12.1. For example, in this chapter, we will use volumetric analysis to find the amount of ethanoic acid (acetic acid) in a sample of vinegar. Before learning the techniques of volumetric analysis, we must first study how chemists express the concentrations of solutions.

Figure 12.1 Volumetric analysis is being used by this laboratory technician in Inniscarra Water Quality Laboratory, Co. Cork, to measure the hardness of water.

12.2 Expressing the concentrations of solutions

You may recall at Junior Cycle that we dissolved copper sulfate in water when making crystals of copper sulfate. The substance that dissolves in the water is called the **solute**. In this case, the solute is copper sulfate. The substance that dissolves the solute is called the **solvent**. In this case, the solvent is water. The solute and solvent together form a perfect mixture which is called a **solution**.

A **solution** is a completely perfect mixture of a solute and a solvent. In a solution, the particles of the solute are uniformly distributed throughout the solvent, i.e. the mixture is homogeneous.

Note that when a solution is formed, it is no longer possible to distinguish between the particles of the solute and the particles of the solvent, Figure 12.2. The word used in the English language to describe this is **homogeneous** (from the Greek 'of the same type') to emphasise that the solution looks the same throughout the flask.

Figure 12.2 All of these solutions of coloured salts in water are perfect mixtures. Note that solutions are always clear. You can no longer see the individual solute and solvent used to make up the solution.

Solutions are always clear, as you can no longer see the individual solute and solvent.

- **Solute:** The **substance that dissolves** in a solvent to form a solution. It is usually present in a smaller amount. For example, in saltwater, **salt (NaCl)** is the solute because it dissolves in the water.
- **Solvent:** The **substance that dissolves the solute**, forming a solution. It is usually present in a larger amount. For example, in saltwater, **water (H_2O)** is the solvent because it dissolves the salt.
- **Solution:** A **homogeneous mixture** of a solute dissolved in a solvent, where the particles are evenly distributed. For example, saltwater is a **solution** because salt (the solute) is completely dissolved in water (the solvent), forming a uniform mixture.

Since there is no boundary between the particles (salt ions and water molecules) in a salt water solution, we say that they are in the same phase or homogeneous. Although the most common type of solution is where the solute is a solid and the solvent is a liquid, solutes and solvents can be solids, liquids or gases.

- If there is a large amount of solute relative to the quantity of solvent, the solution is said to be **concentrated**.
- If there is only a small amount of solute relative to the quantity of solvent, the solution is said to be **dilute**.
- Chemists often need to know the exact amount of solute present in a certain volume of solution. A chemist who is analysing polluted water, for example, must very accurately measure the quantity of oxygen dissolved in the water.

The precise amount of solute in a given amount of solution is referred to as the **concentration** of the solution.

The **concentration** of a solution is the amount of solute that is dissolved in a given volume of solution.

There are a number of different ways of expressing the concentration of a solution.

12.2.1 Percentage of solute

This method of expressing concentration is used for many household solutions as well as in the areas of biochemistry and medicine, Figure 12.3.

There are three ways in which the percentage of solute in a solution is expressed:

1. Weight per weight (w/w)

- A solution labelled 10% w/w NaCl means that there are 10 g of sodium chloride per 100 g of solution.
- This solution is made up by weighing out 10 g of the salt, dissolving it in water, and then adding more water until the total mass of the solution is 100 grams.

This can also be summarised by the formula:

$$\frac{\text{Mass of NaCl}}{\text{Total mass of solution}} \times 100 = \frac{10\text{ g}}{100\text{ g}} = 10\%\text{ w/w}$$

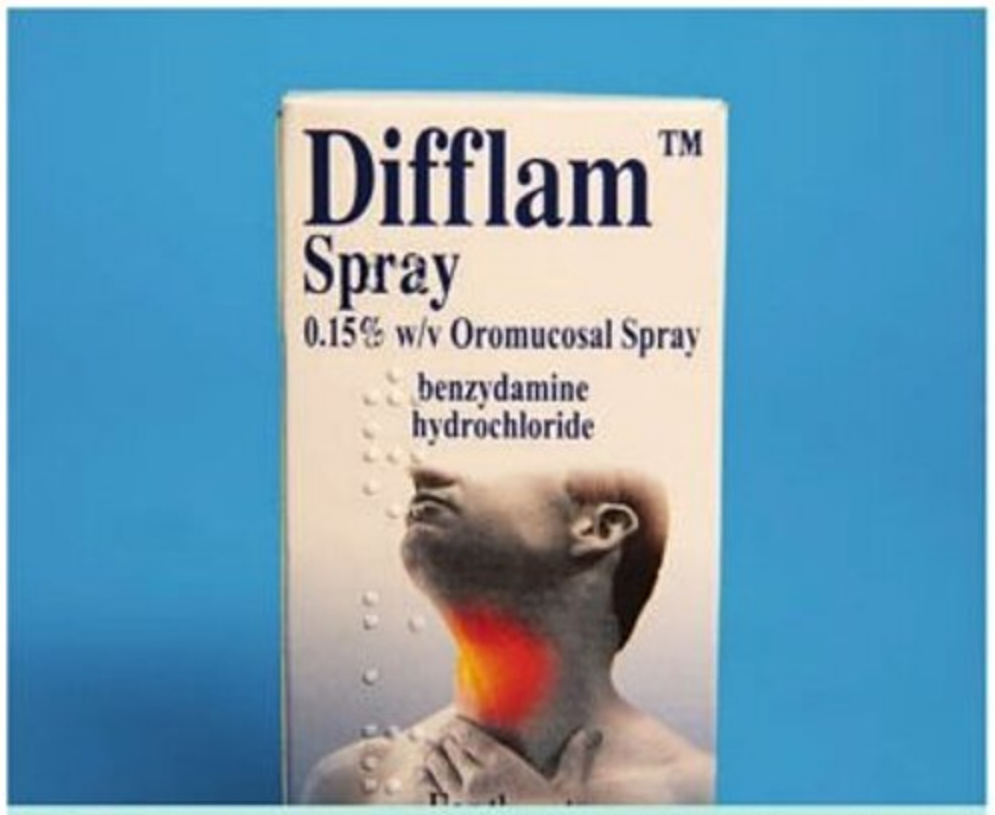


Figure 12.3 Note that the concentration of the active ingredient in this medicine is given as % w/v.

2 Weight per volume (w/v)

- A solution labelled 10% w/v NaCl means that there are 10 g of sodium chloride per 100 cm^3 of solution.
- This solution is made up by weighing out 10 g of the salt, dissolving it in water, and then adding more water until the total volume of the solution is 100 cm^3.
- The concentration of glucose solution is usually stated as % w/v, Figure 12.4.

  This can also be summarised by the formula:

$$\frac{\text{Mass of NaCl}}{\text{Total volume of solution}} \times 100 = \frac{10\text{ g}}{100\text{ cm}^3} = 10\%\text{ w/v}$$

Figure 12.4 Patients are often fed glucose intravenously. The glucose solution is normally about 4% w/v concentration.

3. Volume per volume (v/v)

- This method of expressing concentration involves a liquid solute dissolved in a liquid solvent, i.e. the solution is made from two liquids.
- A solution of ethanol marked 10% v/v has 10 cm^3 of ethanol per 100 cm^3 of solution.
- This solution is made up by measuring out 10 cm^3 of ethanol, adding it to water, and then adding more water until the volume of the solution is 100 cm^3.

  This can also be summarised by the formula:

$$\frac{\text{Volume of alcohol}}{\text{Total volume of solution}} \times 100 = \frac{10\text{ cm}^3}{100\text{ cm}^3} = 10\%\text{ v/v}$$

- The amount of alcohol in alcoholic drinks is usually given in terms of percentage (v/v), e.g. beer and cider are about 4–5% v/v, wine is 10–12% v/v, sherry is 20% v/v, and spirits (whiskey, gin and vodka) have an alcohol content of 40% v/v, Figure 12.5. The high concentration of alcohol in spirits explains why drinking spirits is particularly harmful to your health. Alcohol is a toxic substance, and when consumed, it must be broken down in the liver and removed from the body. However, the liver can only metabolise a limited amount per hour, so excessive drinking can harm your health in many ways, including liver damage, impaired brain function, and long-term health risks such as liver cirrhosis and addiction.

Figure 12.5 Due to the high % v/v of alcohol in spirits, drinking spirits is particularly harmful to your health.

Example 12.1

Question

Some illnesses can upset the salt balance in the body and it may be necessary for a doctor or nurse to administer salt intravenously. The solution of salt that is injected is marked 0.85% w/v. What mass of sodium chloride is needed to make up 250 cm^3 of this solution?

Answer

0.85% w/v means that there are 0.85 g NaCl per 100 cm^3 solution.

Therefore, there are $0.85 \times 2.5 = 2.125$ g NaCl per 250 cm^3 solution.

Answer: 2.125 g NaCl

Example 12.2

Question

65 g of a solution contains 8 g of solute. Express the concentration of this solution as % w/w.

Answer

$$\%\ w/w = \frac{\text{Mass of solute}}{\text{Total mass of solution}} \times 100 = \frac{8\ g}{65\ g} \times 100 = 12.31\%\ w/w$$

12.2.2 Parts per million (ppm)

This method of expressing the concentration of a solution is only used for very dilute solutions. It is particularly useful in water analysis, where you are dealing with very low concentrations of certain substances, perhaps only a few milligrams of a substance in a litre of water, Figure 12.6.

1 mg per litre = 1 mg per 1000 grams of water (the density of water is $1 g/cm^3$)

= 1 mg per 1000 × 1000 mg of water

= 1 mg per million mg

= 1 ppm

In other words, **1 ppm = 1 mg/L**

Irish still spring water.
SERVING SUGGESTION
Best served chilled.
STORAGE Store in a cool, dry place away from direct sunlight, strong odours and chemicals. Once opened, keep refrigerated and consume within 3 days.
Best before end: see neck of bottle.
Warning Choking risk.
The cap is not suitable for children under 36 months.
Do not re-use cap or bottle.
COMPOSITION
Typical values
Per litre
Calcium 110.0mg
Magnesium 31.0mg
Potassium 0.7mg
Sodium 10.0mg
Bicarbonate 340.0mg
Sulphate 14.0mg
Nitrate 6.0mg
Chloride 20.0mg
pH (at source)
Recycling
BOTTLE Widely Recycled
Cap On
Produced in Ireland for Tesco Ireland Ltd., Gresham House, Marine Road, Dun Laoghaire, Co. Dublin.
© Tesco 2023. SC4104
2Le
Bottled at source

Figure 12.6 Expressing concentrations in parts per million (mg/L) is used when the amounts present are very small.

For example, a chemist may report that the concentration of chlorine in water is 2 ppm. This means that there are two milligrams of chlorine per litre of water.

Example 12.3

Question

On analysing a sample of water, a chemist found that 100 cm^3 of it contain 0.005 g of calcium carbonate. What is the concentration of calcium carbonate in ppm?

Answer

0.005 g per 100 cm^3 = 0.005 × 10 g per litre

= 0.05 g /L

= 0.05 × 1000 mg/L

= 50 mg/L

= 50 ppm

Answer: 50 ppm

TEST YOURSELF: Attempt Questions 12.1–12.2 and W12.1–W12.2.

12.2.3 Moles of solute per litre of solution (molarity)

The most important method of expressing the concentration of a solution is in terms of moles of solute per litre of solution. This is called the **molarity** of the solution.

The **molarity** of a solution is the number of moles of solute per litre of solution.

- The symbol for molarity is **M** or **mol/L** (moles per litre).
- It is more usual to use the symbol M instead of mol/L. Therefore, if a solution contains 1 mole of solute per litre of solution, we say that the concentration of the solution is 1 M or 1 mol/L.
- In the S.I. system of units, the symbol mol/L is recommended rather than M. However, since the term *molarity* and its symbol M are used so widely in industry and at third level, it is important for students to realise that the two terms are identical, i.e. **1 M NaOH = 1 mol/L NaOH**.

- **Whenever the symbol M is used, always make sure that it is used in conjunction with a chemical formula,** e.g. a 1 M NaOH solution means a sodium hydroxide solution that has a concentration of 1 mole per litre. Thus a 1 mol/L solution of sodium hydroxide contains 40 grams of sodium hydroxide (M_r of NaOH = 40) per litre of solution. Since it is important in volumetric analysis to have solutions whose concentrations are **accurately** known, we usually use a flask called a **volumetric flask** when making up solutions, Figure 12.7. The correct procedure for using a volumetric flask to prepare a definite volume of solution will be studied at a later stage.
- Suppose that two moles of sodium hydroxide (80 g) are dissolved in water and the solution is made up to the graduation mark in a 1 litre flask. The concentration of this solution is 2 mol/L or 2 M.
- Similarly, a solution which is marked 0.5 mol/L or 0.5 M will contain only half a mole of sodium hydroxide (20 g) per litre of solution.
- A solution that contains one-tenth of a mole per litre is often said to be **decimolar** (0.1 M), e.g. a decimolar solution of sodium hydroxide contains 4 g (one-tenth of a mole) per litre of solution.

A **1 M (one molar)** solution is one that contains one mole of the solute dissolved in one litre of solution.

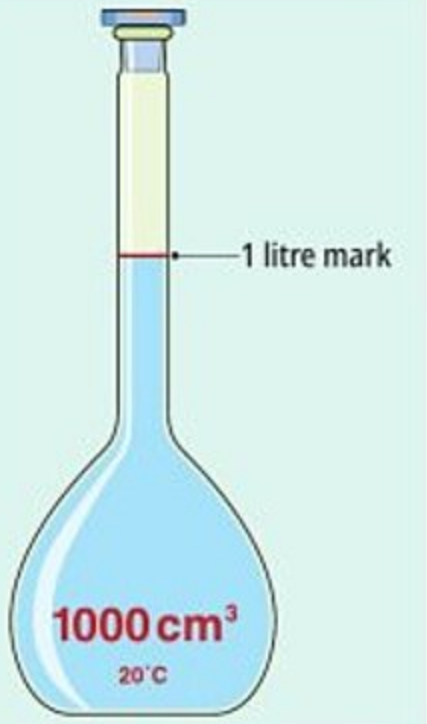


Figure 12.7 If one mole of a substance is dissolved in water and the solution is made up to the litre mark, we have a 1 mol/L (1 molar = 1 M) solution.

12.3 Converting moles per litre to grams per litre

Chemists often find it necessary when carrying out volumetric analysis to convert from concentrations expressed in moles per litre to concentrations expressed in grams per litre. The method of carrying out this conversion is shown in the following examples.

Example 12.4

Question

How many grams of NaCl per litre are present in a solution marked 0.25 M NaCl? (Na = 23, Cl = 35.5)

Answer

Rel. Molecular Mass of NaCl = 23 + 35.5 = 58.5

A 1 M NaCl solution contains 58.5 grams per litre.

∴ a 0.25 M NaCl solution contains 58.5 × 0.25 = 14.625 g/L

Answer: 14.625 grams NaCl per litre.

Example 12.5

Question

Calculate the concentration in grams per litre of bench dilute sulfuric acid whose concentration is 1.5 mol/L. (H = 1, O = 16, S = 32)

Answer

Rel. Molecular Mass of H_2SO_4 = 2(1) + 32 + 4(16) = 98

A 1 M H_2SO_4 solution contains 98 grams per litre.

∴ a 1.5 M H_2SO_4 solution contains 98 × 1.5 = 147 g/L

Answer: 147 grams H_2SO_4 per litre.

12.4 Converting grams per litre to moles per litre (molarity)

This type of calculation is met very often in volumetric analysis. Study the following examples carefully.

Example 12.6

Question

What is the molarity of a solution that contains 3.68 g of NaOH per litre of solution? (H = 1, O = 16, Na = 23)

Answer

Rel. Molecular Mass of NaOH = 23 + 16 + 1 = 40

40 g in 1L solution → 1 M NaOH solution

1 g in 1L solution → $\frac{1}{40}$ M NaOH solution

3.68 g in 1L solution → $\frac{3.68}{40}$ M NaOH solution

= 0.092 M NaOH solution

Answer: 0.092 M NaOH.

Example 12.7

Question

Calculate the concentration in moles per litre of a solution containing 45 grams of sulfuric acid per 250 cm^3 of solution. (H = 1, O = 16, S = 32)

Answer

Rel. Molecular Mass of H_2SO_4 = 2(1) + 32 + 4(16) = 98

98 g H_2SO_4 in 1L solution → 1 M solution

1 g H_2SO_4 in 1L solution → $\frac{1}{98}$ M solution

45 g H_2SO_4 in 1L solution → $\frac{45}{98}$ M solution

45 g H_2SO_4 in 250 cm^3 solution → $\frac{4 \times 45}{98}$ M solution

= 1.84 M

Answer: The concentration of the solution is 1.84 M.

Study the last step of Example 12.7 carefully.

- Since the sulfuric acid is actually dissolved in only 250 cm^3 of solution, the concentration of the solution is four times higher than it would be if it were dissolved in a litre.
- If you find this difficult to understand, studying the dissolving of copper sulfate in water may help, Figure 12.8.
- As the concentration increases the intensity of the colour also increases.

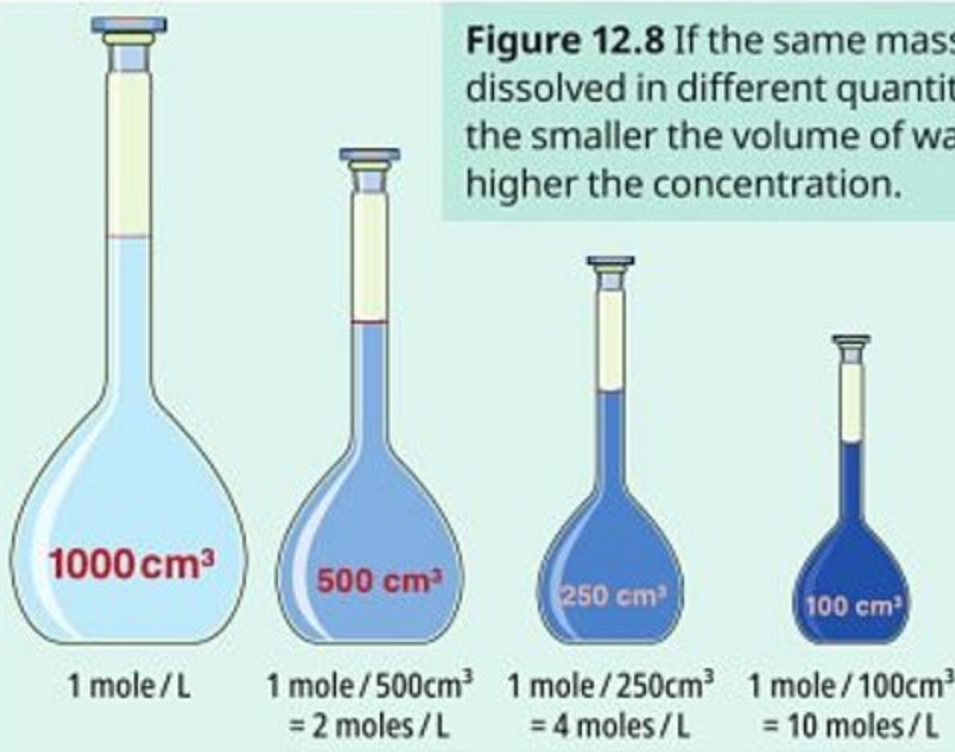


Figure 12.8 If the same mass of solute is dissolved in different quantities of water, the smaller the volume of water, the higher the concentration.

12.5 Using (i) first principles and (ii) a formula to calculate the number of moles given the volume and the molarity of a solution

In all examples studied so far in this chapter, we have worked out the answers from first principles. This means that we solved all the problems using the basic definitions without have to use any formulas. In the next example, we will first solve the problem using first principles and then derive a general formula to help in this type of calculation.

Chemists, having prepared a solution in a volumetric flask, usually take a smaller quantity (e.g. 25 cm^3) of the solution out of the volumetric flask in order to perform various experiments in volumetric analysis. When using this smaller volume, it is necessary to be able to answer questions like that given in Example 12.8.

Example 12.8

Question

How many moles of NaOH are present in 25 cm^3 of 0.55 M NaOH?

Answer

By definition:

1 litre of 0.55 M NaOH contains 0.55 moles NaOH.

i.e. 1000 cm^3 of 0.55 M NaOH contains 0.55 moles NaOH

$\therefore$ 1 cm^3 of 0.55 M NaOH contains moles $\frac{0.55}{1000}$ moles NaOH

$\therefore$ 25 cm^3 of 0.55 M NaOH contains $\frac{25 \times 0.55}{1000}$ moles NaOH

= 0.014 moles NaOH.

Answer: 0.014 moles

In general, if the volume is given in cm^3 and the concentration in molarity (moles per litre), the number of moles may be calculated from the expression:

$$\text{Number of moles} = \frac{\text{volume}^* \times \text{molarity}}{1000}$$

(*in cm^3)

This is a very useful expression and is worth learning off.

Example 12.9

Question

How many moles of hydrochloric acid are present in 30 cm^3 of 0.2 M HCl?

Answer

$$\text{Number of moles of HCl} = \frac{\text{volume} \times \text{molarity}}{1000}$$

$$= \frac{30 \times 0.2}{1000}$$

$$= 0.006 \text{ moles}$$

Answer: 0.006 mol

Example 12.10

Question

What mass of sodium hydroxide is contained in 25 cm^3 of a 0.75 M solution of sodium hydroxide? (H = 1, O = 16, Na = 23)

Answer

$$\text{Number of moles} = \frac{\text{volume} \times \text{molarity}}{1000}$$

$$= \frac{25 \times 0.75}{1000}$$

$$= 0.019 \text{ moles}$$

$$= 0.019 \times 40 \text{ g } (M_r \text{ NaOH} = 40)$$

$$= 0.76 \text{ g}$$

Answer: 0.76 g

Example 12.11

Question

What volume of 0.15 M sodium hydroxide solution will contain 5 grams of sodium hydroxide? (H = 1, O = 16, Na = 23)

Answer

First convert 5 grams to moles.

$$\text{No. of moles of NaOH} = \frac{\text{Mass}}{\text{Rel. Molecular Mass}}$$

$$= \frac{5}{40}$$

$$= 0.125 \text{ moles}$$

Calculate the volume using the formula:

$$\text{No. of moles} = \frac{\text{volume} \times \text{molarity}}{1000}$$

$$0.125 = \frac{\text{volume} \times 0.15}{1000}$$

$$\frac{0.125 \times 1000}{0.15} = \text{volume}$$

i.e. volume = 833.33 cm^3

Answer = 833.33 cm^3

TEST YOURSELF: Attempt Questions 12.3–12.4 and W12.3–W12.5.

12.6 Reaction between a solution and a solid

In a number of chemical reactions, solids react with solutions, e.g. as discussed in Chapter 11, many metals react with acidic solutions. Examples 12.12 and 12.13 (online) show how we can calculate the mass of a solid that reacts with a given volume of solution.

Example 12.12

Question

What mass of magnesium will react with 50 cm^3 of 0.5 M H_2SO_4? The balanced equation for the reaction is:

$$Mg + H_2SO_4 \rightarrow MgSO_4 + H_2$$

Answer

$$\text{No. of moles of acid} = \frac{\text{volume} \times \text{molarity}}{1000}$$

$$= \frac{50 \times 0.5}{1000}$$

$$= 0.025 \text{ moles}$$

From the balanced equation, one mole of sulfuric acid reacts with one mole of magnesium. Therefore, moles of magnesium which react:

$$= 0.025$$

$$= 0.025 \times 24 \text{ g Mg}$$

$$= 0.6 \text{ g}$$

Answer: 0.6 g magnesium.

TEST YOURSELF: Attempt Questions 12.5 and W12.6–W12.7.

Study Example 12.13 in the online resources.

12.7 Dilution of solutions

Many common laboratory reagents are purchased as solutions of high concentration, e.g. the concentration of sulfuric acid supplied to laboratories is 18 M. Some of the common laboratory reagents and their concentrations as supplied are given in Table 12.2.

Substance	Concentration
Sulfuric acid	18 M
Nitric acid	16 M
Hydrochloric acid	12 M
Ammonia	16 M
Ethanoic acid (acetic acid)	17 M

Table 12.2 The concentrations of common reagents as supplied to laboratories.

- For most laboratory experiments, these reagents must be used in their diluted state, e.g. the concentration of 'bench' dilute hydrochloric acid and 'bench' dilute ammonia is only 3 M approx.
- When a solution is diluted, more solvent is added but the quantity of solute is unchanged.
- Since the volume of the solution increases and the same number of moles is present, then the concentration of the solution must decrease, Figure 12.9.

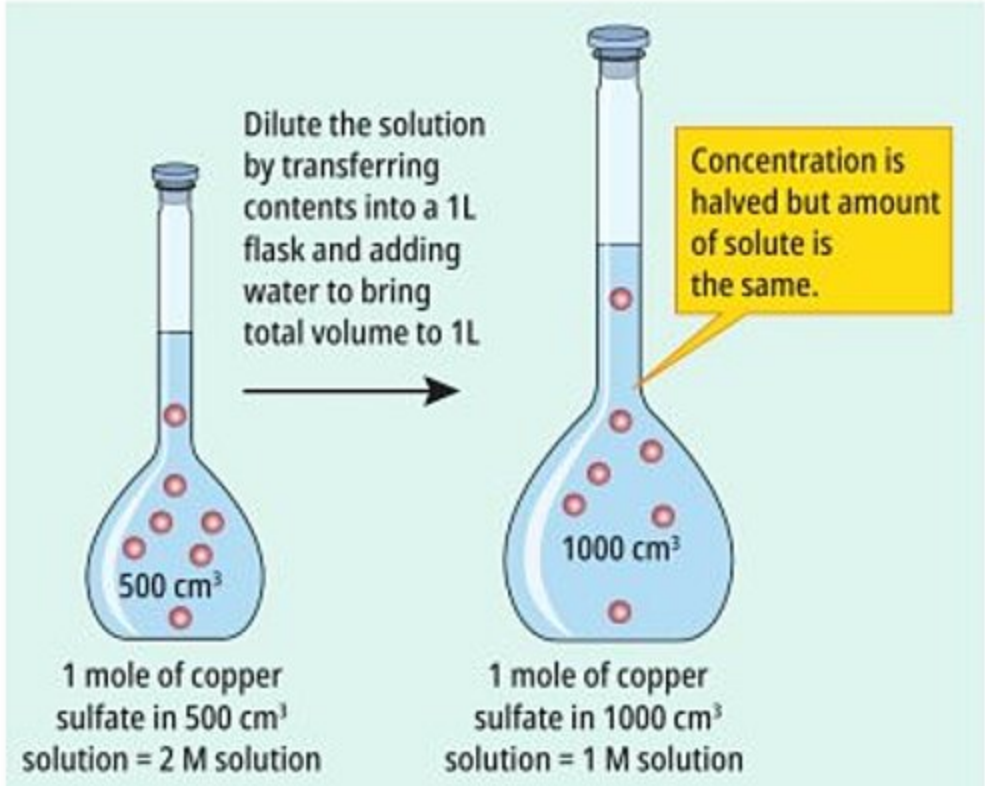

Dilute the solution by transferring contents into a 1L flask and adding water to bring total volume to 1L
Concentration is halved but amount of solute is the same.
500 cm³
1000 cm³
1 mole of copper sulfate in 500 cm³ solution = 2 M solution
1 mole of copper sulfate in 1000 cm³ solution = 1 M solution

Figure 12.9 Adding water does not affect the amount of solute present but does reduce the concentration of the solution.

In order to dilute a concentrated solution to give a dilute solution of known concentration, it is important to remember that the number of moles of solute in the diluted solution is the same as the number of moles of solute in the concentrated solution.

No. of moles of solute in diluted solution = No. of moles of solute in concentrated solution

$$\text{i.e. } \frac{Vol_{dil}^{*} \times M_{dil}}{1000} = \frac{Vol_{conc}^{*} \times M_{conc}}{1000}$$

(*in cm^3)

We use this relationship to solve problems on dilution as shown in Examples 12.14 and 12.15 (online).

Note: It does not matter what units are used to express the concentration, as long as the same units are used on each side of the equation.

Example 12.14

Question

What volume of 12 M HCl solution is required to make up 500 cm^3 of 3 M HCl solution?

Answer

No. of moles of solute in diluted solution = No. of moles of solute in concentrated solution

$$\text{i.e. } \frac{Vol_{dil} \times M_{dil}}{\cancel{1000}} = \frac{Vol_{conc} \times M_{conc}}{\cancel{1000}}$$

$$500 \times 3 = Vol_{conc} \times 12$$

$$Vol_{conc} = \frac{500 \times 3}{12}$$

$$Vol_{conc} = 125\ cm^3$$

Answer: 125 cm^3 of the concentrated acid would have to be diluted to 500 cm^3.

» Study Example 12.15 in the online resources.

Serial dilution

So far we have studied examples of simple dilutions. A simple dilution is a single-step dilution where a concentrated solution is mixed with a solvent (usually deionised water) to achieve the required concentration. However, in some cases we may need a range or series of solutions. For example, chemists may need to test the effectiveness of a new drug using a series of different concentrations of the drug. To do this, we carry out a procedure where a solution is repeatedly diluted by a constant factor in a number of steps. This process is called a **serial dilution** (also called series dilution).

Serial dilution is a step-by-step dilution process where a solution is diluted multiple times in a systematic way. Each step reduces the concentration of the original solution by the same factor (e.g. commonly 1:10).

Serial dilutions are very useful in chemistry to produce a series of solutions whose concentrations are accurately known. These solutions have many uses in chemistry. For example, these solutions may be used to calibrate an instrument called a colorimeter, Figure 12.10. (Calibration is the process of making sure that the instrument will produce accurate results.)

Figure 12.10 This colorimeter is being used to measure the amount of chlorine in swimming pool water. The instrument must first be calibrated using a series of solutions of known concentration of chlorine. A sample of the swimming pool water of unknown concentration is then placed in the colorimeter and the concentration of chlorine can then be easily determined.

Note that in the definition of serial dilution, we referred to the ongoing dilution of the original solution by the same factor each time. This is commonly called the **dilution factor**.

For example, in a 1:10 dilution, 1 cm^3 of the solution is mixed with 9 cm^3 of the solvent. In other words, the dilution factor is 10.

$$\text{Dilution factor} = \frac{\text{Total volume}}{\text{Volume of stock solution}} = \frac{10\ cm^3}{1\ cm^3} = 10$$

The **dilution factor** is the ratio of the volume of the original solution to the total volume after dilution.

The key idea about serial dilutions is illustrated in Figure 12.11.

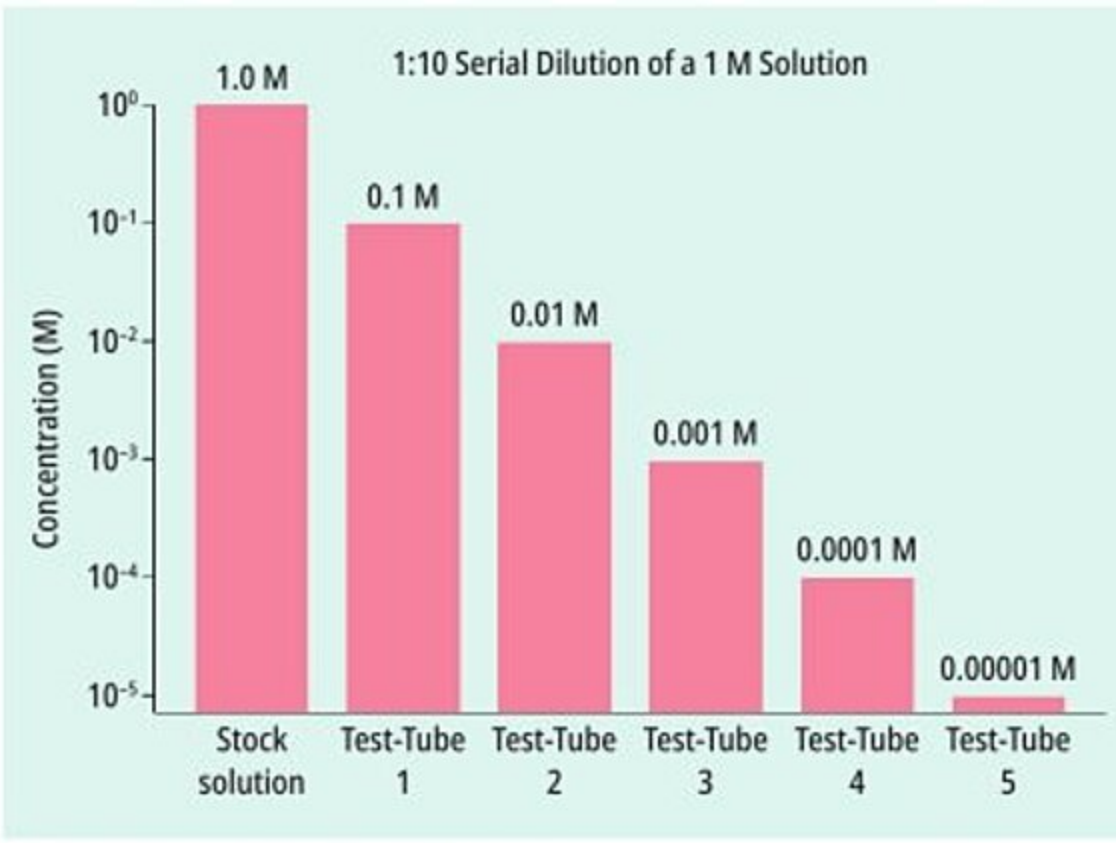


Figure 12.11 Diagrammatic representation of changes in concentration resulting from a 1:10 dilution of a 1 M solution.

Example 12.16

Question

If you perform three consecutive dilutions of 1:10, what is the dilution factor?

Answer

Dilution factor = 10 × 10 × 10 = 1000

Example 12.17

Question

A solution containing 150 g/L is diluted twice by 1:10 and once by 1:5. What is the final concentration of the solution in grams per litre?

Answer

Step 1

After one dilution 1:10 the concentration will be 15 g/L.

Step 2

After the second dilution of 1:10 the concentration will be 1.5 g/L.

Step 3

After the third dilution of 1 : 5 the concentration will be 0.3 g/L.

12.1 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 5 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 5

To prepare a series of 1:10 serial dilutions of a stock potassium permanganate, $KMnO_4$, solution and investigate how the concentration decreases at each step

Note that potassium permanganate is also called potassium manganate(VII).
We will explain the origin of this name in Chapter 14.

Introduction

In this experiment, we will investigate how to perform a number of simple dilutions to produce a range of solutions of different concentrations. We will use a dilution factor of 1:10. In other words, the concentration of each diluted solution is one-tenth of the concentration of the solution from which it has been made. The source of solution to be diluted comes from the diluted solution of the previous step. The key steps involved in a serial dilution are summarised in Figure 12.12.

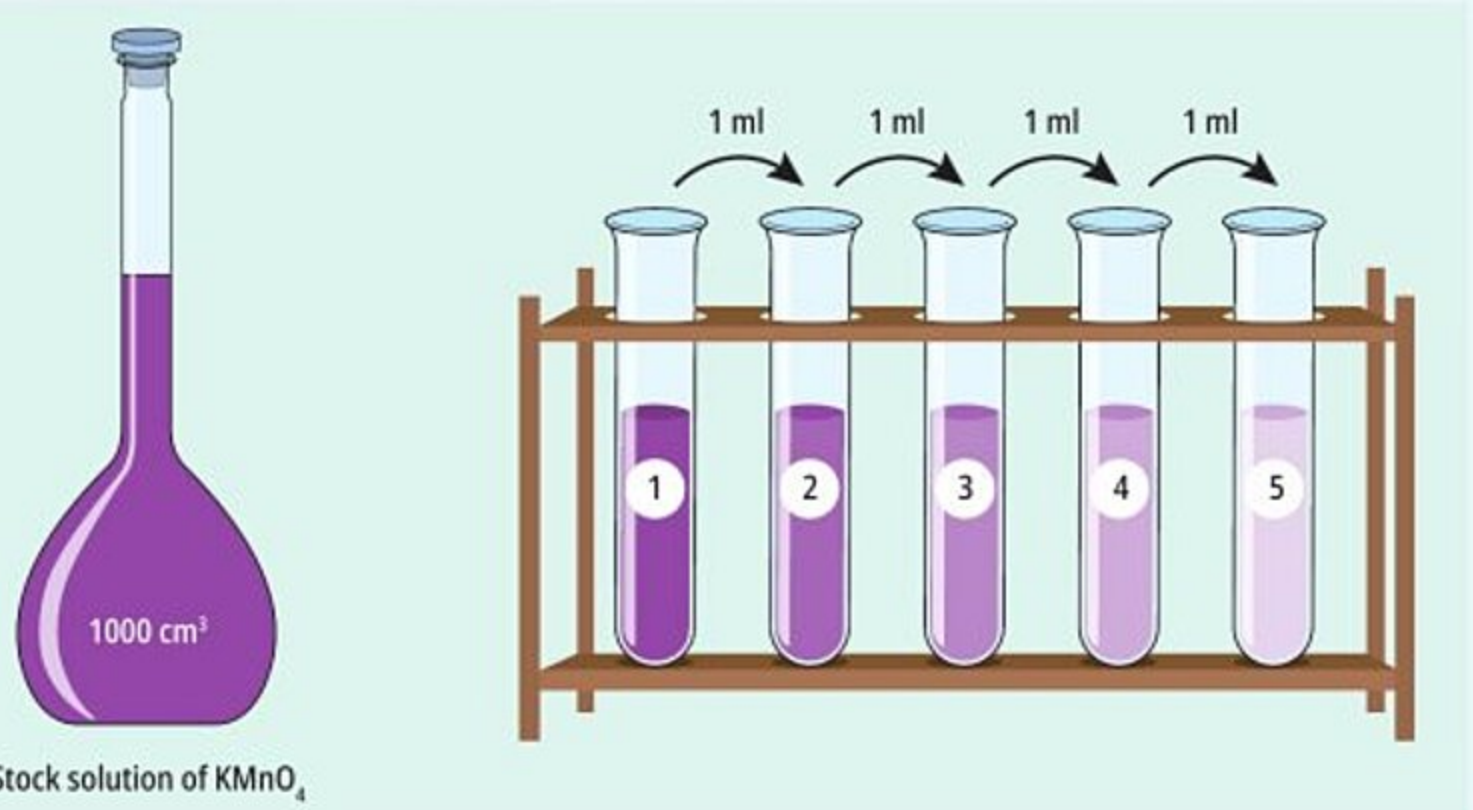


Figure 12.12 In a serial dilution, the concentration of each diluted solution is a fraction of the concentration of the solution from which it has been made. In the example shown, the dilution factor is 1:10.

Key steps in procedure

1. Using a graduated dropper (also called a graduated Pasteur pipette), a volume of 9 cm^3 of deionised water is placed in each of five test-tubes. The graduated Pasteur pipettes are usually graduated up to 3 cm^3.
2. Each test-tube is labelled 1 to 5. Some of the stock solution is poured into a small beaker. A graduated dropper is used to transfer 1 cm^3 of the stock 0.05 M $KMnO_4$ solution from the beaker into test tube 1. (Dilution 1).
3. Test-tube 1 is gently shaken to ensure a homogeneous mixture.
4. A clean graduated dropper is used to transfer 1 cm^3 of the dilute $KMnO_4$ solution from test-tube 1 to test-tube 2. (Dilution 2).
5. Test-tube 2 is gently shaken to ensure a homogeneous mixture.
6. A clean graduated dropper is used to transfer 1 cm^3 of the dilute $KMnO_4$ solution from test-tube 2 to test-tube 3. (Dilution 3).
7. Test-tube 3 is gently shaken to ensure a homogeneous mixture.
8. A clean graduated dropper is used to transfer 1 cm^3 of the dilute $KMnO_4$ solution from test-tube 3 to test-tube 4. (Dilution 4).
9. Test-tube 4 is shaken to ensure a homogeneous mixture.
10. A clean graduated dropper is used to transfer 1 cm^3 of the dilute $KMnO_4$ solution from test-tube 4 to test-tube 5. (Dilution 5).
11. Test-tube 5 is shaken to ensure a homogeneous mixture.

Observation

- The colour of the diluted solution in each test-tube is a lighter shade of purple compared to the solution from which it has been made.

Conclusion

- Since we started with a 0.05M solution, we have made a series of solutions of concentration 0.005M (in test-tube 1), 0.0005M (in test-tube 2), 0.00005M (in test-tube 3), 0.000005 M (in test-tube 4) and 0.0000005 M (in test-tube 5). This is illustrated in Figure 12.12.

In Experiment 12.1, we used a 1:10 dilution. If for example, the dilution is 1:2, then we would add 1 cm^3 of solution to 1 cm^3 of water in each test-tube. Therefore, if you started with, say, a 1M solution, the resulting concentrations would be 0.5 M, 0.25 M, 0.125 M and 0.0625 M.

TEST YOURSELF: Attempt Questions 12.6 and W12.8–W12.11.

12.8 Standard solutions

A **standard solution** is a solution whose concentration is accurately known.

When carrying out laboratory practical work, we often have to use solutions of exactly known concentrations. Such solutions are called standard solutions, e.g. a solution containing 4.65 grams of sodium chloride per litre is a standard solution.

A standard solution is prepared by dissolving a definite, precisely known mass of solute in a suitable solvent (usually deionised water) to give a definite, precisely known volume of solution.

- The concentration of a solution may be determined either by preparing the solution ourselves or by finding the concentration of the solution by analysis.
- Since many substances cannot be obtained in a high degree of purity, it is not possible for chemists to make up a wide range of standard solutions by simply dissolving a weighed amount of solute and making the solution up to a precise volume. For example, it is not possible to weigh out a precise quantity of sulfuric acid because sulfuric acid absorbs moisture from the air. Similarly, an accurately known quantity of iodine cannot be weighed out because iodine tends to sublime (change to a vapour) at room temperature.

In order to make up standard solutions, chemists need substances with several characteristics. Ideally, they should be very pure, stable in air, soluble in water to give stable solutions, and, if possible, have high relative molecular masses in order to minimise percentage error. Such substances are called **primary standards**.

A primary standard is a substance that meets the criteria summarised in Table 12.3.

	Criteria for primary standard
1.	It must be available in a highly pure state.
2.	It must be stable in air, e.g. it should not lose water of crystallisation to the air (efflorescence) or absorb water from the air (be deliquescent or hygroscopic).
3.	It must dissolve easily in water.
4.	It should have a fairly high relative molecular mass (so that the precision in weighing out a known mass is as high as possible).
5.	When used in volumetric analysis, it should undergo complete and rapid reaction.
6.	If possible, it should not be hydrated, i.e. it must be anhydrous (have no water of crystallisation).

Table 12.3 A primary standard must meet the criteria specified in this table.

Therefore, a primary standard may be defined as follows:

A **primary standard** is a substance that can be obtained in a stable, pure and soluble solid form so that it can be weighed out and dissolved in water to give a solution of accurately known concentration.

Many common chemicals cannot be considered as primary standards, Table 12.4.

Substance	Why is it not a primary standard?
Sulfuric acid	It is hygroscopic, i.e. it absorbs water from the air.
Hydrochloric acid	HCl is a gas at room temperature and difficult to weigh out accurately.
Sodium hydroxide	It is deliquescent, i.e. it absorbs enough water from the air to form a solution.
Hydrated sodium carbonate	It effloresces, i.e. it loses water of crystallisation to the air.
Iodine	It sublimes at close to room temperature.
Potassium permanganate	It is not available in a pure state and it is not stable, e.g. its solutions deteriorate if exposed to light.

Table 12.4 Many common chemicals do not match the requirements for primary standards.

Only a small number of common substances satisfy the above criteria and are classed as primary standards, e.g. anhydrous sodium carbonate, Na_2CO_3 and sodium chloride, NaCl. Standard solutions are widely used in industry and in research, and so it is important to be able to prepare them. So let's get started on preparing a standard solution!

12.2 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 6 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 6

To prepare a standard solution of sodium carbonate

Introduction

In this experiment, an accurately known amount of anhydrous sodium carbonate is weighed, dissolved in water and then the solution is made up to a known volume. Since anhydrous sodium carbonate is a primary standard, the concentration of the solution will be known precisely, i.e. we are using a primary standard to make up a standard solution.

Key steps in procedure

- A known mass of anhydrous sodium carbonate is accurately weighed out on a clock glass using the laboratory balance.
- The anhydrous sodium carbonate is added to a beaker containing deionised water.
- A wash bottle of deionised water is used to wash all traces of the sodium carbonate from the clock glass into the beaker.
- The mixture is stirred with a clean glass rod until the solid dissolves completely.
- The solution is transferred to a clean 250 cm^3 volumetric flask using a funnel and glass rod, Figure 12.13.
- All traces of the solution are washed from the beaker, rod and funnel into the volumetric flask using deionised water. The funnel is removed.

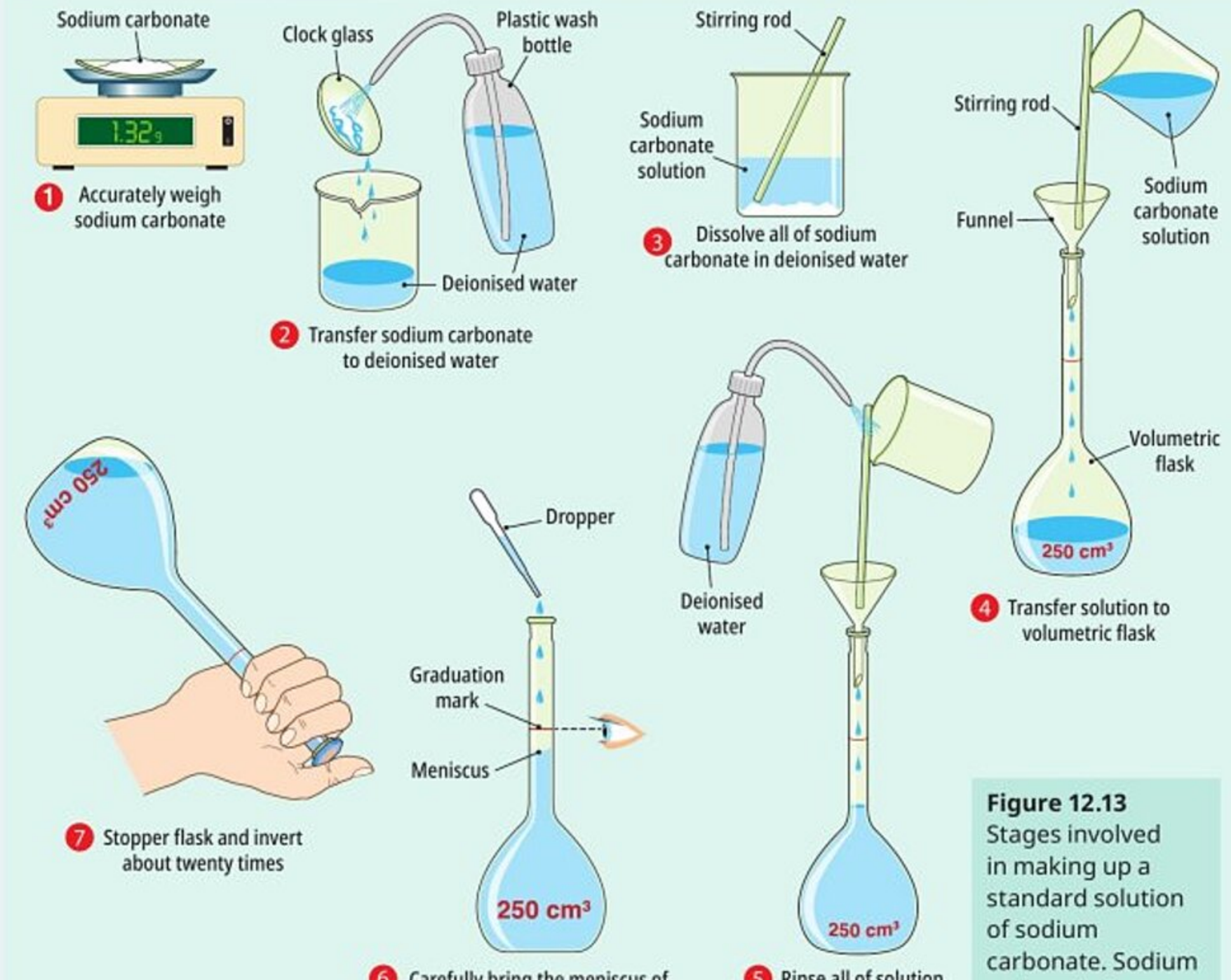


Figure 12.13 Stages involved in making up a standard solution of sodium carbonate. Sodium carbonate is an example of a primary standard.

- Deionised water is added to the volumetric flask until the bottom of the meniscus of the liquid is exactly level with the graduation mark, Figure 12.14. Towards the end, the water is added slowly using a dropper. The volumetric flask must be placed on a level surface. The bottom of the meniscus must be viewed at eye-level.
- The mark on the neck of the flask should be viewed at eye-level to ensure that the bottom of the meniscus of the liquid coincides with it.
- The stoppered flask is inverted about 20 times to mix the contents thoroughly (homogeneous mixture).

The concentration (in moles per litre) of the solution is then calculated. The calculation involved is similar to that in Example 12.7.

We now have a solution whose concentration is known precisely, i.e. a standard solution of sodium carbonate.

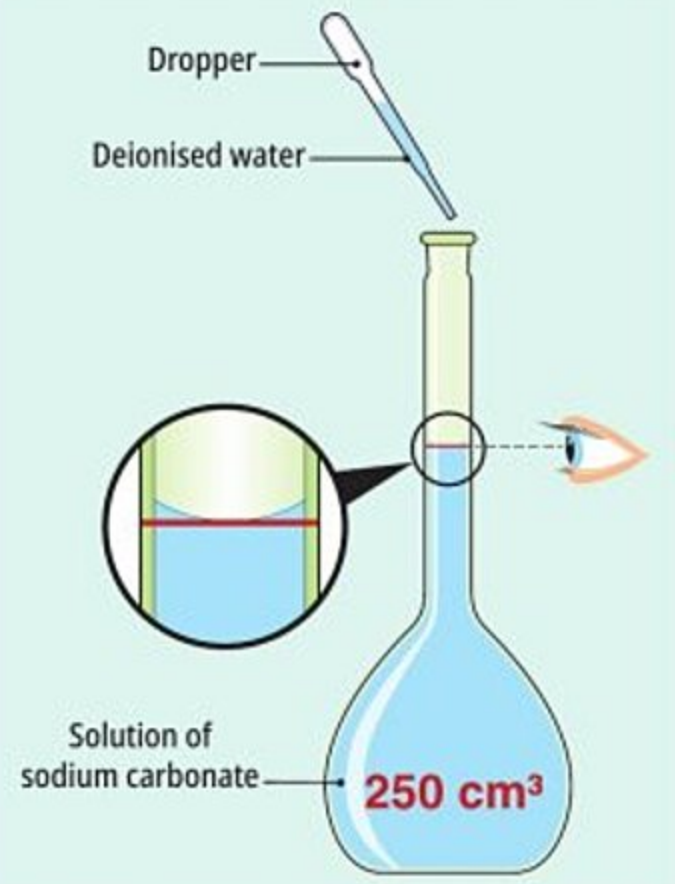


Figure 12.14 The bottom of the meniscus must be brought up to the graduation mark using a dropper.

EXAM TIP!

When answering exam questions on the procedure for making up standard solutions, pay particular attention to giving precise details:

1. Do not forget to mention that you used **deionised** water. Ordinary tap water contains many dissolved substances that could interfere with the solution and affect the results of the experiment.
2. Always mention that deionised water is added until the **bottom** of the meniscus is on the graduation mark of the volumetric flask and the reading taken at eye-level.
3. It is important that you use the term **inverted** (not 'shaken') as merely shaking the volumetric flask would not mix the contents sufficiently.

Example 12.18

Question

5.28 grams of anhydrous sodium carbonate, Na_2CO_3, were weighed out and made up to 250 cm^3 of solution. Calculate the molarity of the solution.

Answer

We can solve this from first principles using the basic definition of a 1 M solution.

1 mole Na_2CO_3 in 1 litre of solution → 1 M Na_2CO_3 solution

i.e. 106 g Na_2CO_3 in 1 litre of solution → 1 M Na_2CO_3 solution (M_r Na_2CO_3 = 106)

$$1\text{g } Na_2CO_3 \text{ in 1 litre of solution} \rightarrow \frac{1}{106} \text{ M } Na_2CO_3 \text{ solution}$$

$$5.28\text{ g } Na_2CO_3 \text{ in 1 litre of solution} \rightarrow \frac{1 \times 5.28}{106} \text{ M } Na_2CO_3 \text{ solution}$$

$$5.28\text{ g } Na_2CO_3 \text{ in } \mathbf{250\ cm^3} \text{ of solution} \rightarrow \frac{4 \times 5.28}{106} \text{ M } Na_2CO_3 \text{ solution}$$

$$= 0.199 \text{ M } Na_2CO_3 \text{ solution}$$

Answer: 0.199 M

DIGITAL: A video of this experiment is available on FolensHIVE.

12.9 Volumetric analysis apparatus

- **Volumetric analysis** involves reacting together volumes of solutions.
- In volumetric analysis, the concentration of a solution is determined by reacting that solution with another solution of known concentration (standard solution).
- A definite volume (usually 25 cm^3) of one of the solutions is taken and the other solution is added slowly until the two solutions have reacted completely.
- This procedure is known as a **titration**.
- The stage when the two solutions **just** react completely with each other is called the **equivalence point** of the titration.
- When the equivalence point is shown by an indicator it is called the **end point** of the titration.

A **titration** is a laboratory procedure where a measured volume of one solution is added to a known volume of another solution until the reaction is complete.

In chemistry, the chemical which is being analysed in an experiment is called the **analyte**.

The **analyte** is the chemical species being analysed to determine its concentration, identity or properties.

For example, in a titration of vinegar against a solution of known concentration, the ethanoic acid (acetic acid) in the vinegar is the analyte. In the photograph shown at the beginning of this chapter where the hardness of water is being measured, the analyte is calcium and magnesium ions. In measuring the amount of salt in a saline solution, the analyte is sodium chloride.

In volumetric analysis, titrations are performed to determine the concentration of analytes in solution. These concentrations are determined by titration using primary standard solutions or solutions that have been standardised using primary standards.

Before studying the correct procedure for performing a titration, we shall study the apparatus that is used in volumetric analysis. One of the advantages of volumetric analysis is that the apparatus required is fairly simple. The main apparatus used in volumetric analysis consists of (i) the beaker, (ii) the graduated cylinder, (iii) the volumetric flask, (iv) the pipette, (v) the burette and (vi) the conical flask.

Graduation marks on these instruments may be written in cubic centimetres (cm^3) or in millilitres (ml). A cm^3 is exactly the same as a ml.

A detailed description of each item of apparatus is given in the Laboratory Notebook accompanying this textbook.

12.10 Procedure in carrying out a titration

Because of the importance of volumetric analysis, it is vital that you master the technique involved in carrying out a titration accurately. This technique is described in detail in Student Experiment 12.3 in your Laboratory Notebook along with some important precautions to take. The main stages in carrying out a titration will now be outlined.

12.3 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 7 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 7

To use the standard solution of sodium carbonate solution prepared in the previous experiment to standardise a given hydrochloric acid solution

Introduction

Sodium carbonate is a base that reacts with hydrochloric acid according to the equation:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

Essentially, what is happening is that the carbonate ion is accepting two protons from the hydrochloric acid to form carbon dioxide and water:

$$CO_3^{2-} + 2H^+ \rightarrow H_2O + CO_2$$

By titrating the given hydrochloric acid solution against a known volume of sodium carbonate solution whose concentration is accurately known, we can determine the concentration of the hydrochloric acid solution. An indicator (methyl orange in this case) is used to find the end point of the titration.

Note: In acid–base titrations, the acid is usually placed in the burette and the base in the conical flask ('**A**cid **A**bove, **B**ase **B**elow'). One of the main reasons for this is that some common bases (e.g. sodium hydroxide), if placed in a burette would cause the tap to stick. Sodium hydroxide solution attacks glass, especially the ground glass surfaces in some burette taps. Also, it absorbs carbon dioxide from the air and forms a crust of sodium carbonate around the tap – this happens even with the modern plastic taps. Both of these actions cause the burette taps to seize up.

Key steps in procedure

- The pipette, burette and conical flask are washed with deionised water.
- The pipette is rinsed with sodium carbonate solution.
- The burette is rinsed with hydrochloric acid solution.

- 25 cm^3 of the sodium carbonate solution are pipetted from a beaker into the conical flask, Figure 12.15. The beaker should have been perfectly dry before pouring the sodium carbonate solution into it from the volumetric flask.
- A few drops of methyl orange indicator are added to the sodium carbonate solution in the conical flask.

Observation

The methyl orange indicator in the conical flask is a yellow colour as it is in a basic (alkaline) solution.

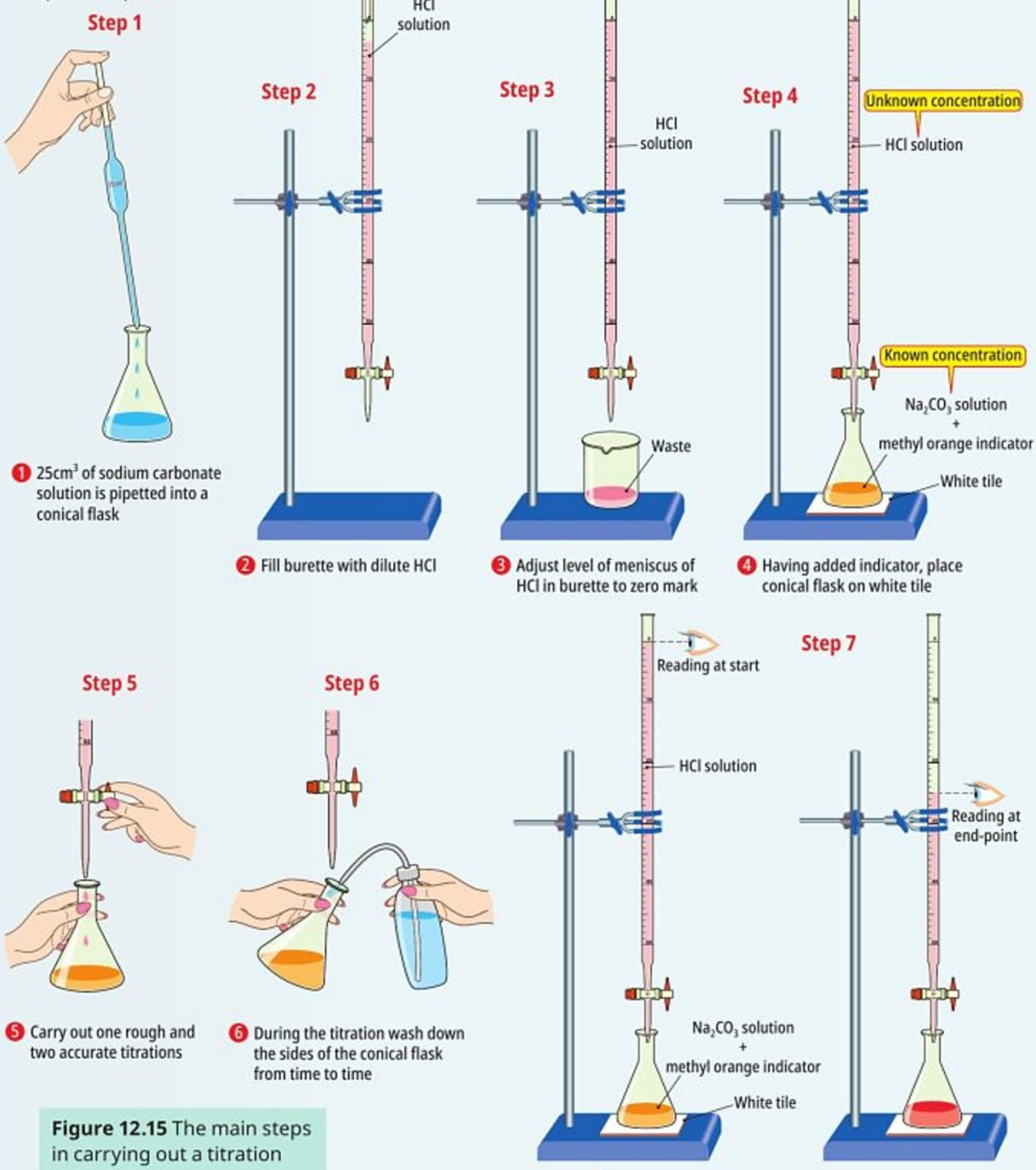

Step 1
Step 2
HCl solution
Step 3
HCl solution
Waste
Step 4
Unknown concentration
HCl solution
Known concentration
Na_2CO_3 solution
+
methyl orange indicator
White tile
1 25cm³ of sodium carbonate solution is pipetted into a conical flask
2 Fill burette with dilute HCl
3 Adjust level of meniscus of HCl in burette to zero mark
4 Having added indicator, place conical flask on white tile
Step 5
Step 6
Step 7
Reading at start
HCl solution
Reading at end-point
Na_2CO_3 solution
+
methyl orange indicator
White tile
5 Carry out one rough and two accurate titrations
6 During the titration wash down the sides of the conical flask from time to time
7 When the indicator has just changed colour, stop the titration and note the volume of acid added

Figure 12.15 The main steps in carrying out a titration

Procedure (continued)

- The burette is clamped vertically using the retort stand (or burette stand) and is filled through a funnel with the dilute hydrochloric acid solution to above the zero mark.
- The funnel is removed from the burette.
- The tap of the burette is opened to fill the tap and the space below the tap with the solution.
- The level of hydrochloric acid solution is adjusted until the bottom of the meniscus is level with the zero graduation mark, taking the reading at eye level.
- A white tile is placed on the base of the retort stand and the conical flask is placed on the white tile.
- Using the thumb and first two fingers of the left hand, the tap of the burette is opened. The acid is allowed to run fairly quickly into the conical flask.
- The conical flask is continuously swirled with the right hand.
- The titration is stopped from time to time and the sides of the conical flask are washed down with deionised water from the wash bottle.

Explanation

- Only a small volume of indicator should be added. This is because acid–base indictors are either weak acids or weak bases themselves, and if too much is added it could lead to a significant inaccuracy in the result of the titration.
- Methyl orange is suitable because we are titrating a strong acid against a weak base. This will be explained in more detail in Chapter 19.
- The purpose of the white tile is to enable us to detect colour changes more clearly.
- Washing down the side of the flask ensures that no drops of acid are stuck to the side of the flask. It is important that all of the acid added from the burette reacts with the sodium carbonate.
- Deionised water may be added to the conical flask at any stage of the titration. It does not affect the amount of sodium carbonate in the conical flask. A volume of 25 cm^3 of the sodium carbonate solution has been pipetted into the conical flask. This volume of sodium carbonate contains a certain number of moles of sodium carbonate. Whether we now add 10 cm^3 or 100 cm^3 of deionised water to the conical flask, this will not affect the number of moles of sodium carbonate present in the conical flask.
- Note the distinction between washing out the pipette and burette with the solutions which they contain and **not** washing out the conical flask with the solution it is about to contain. In the case of adding water to the conical flask during the titration, the dilution occurs **after** the required amount of sodium carbonate solution has already been measured and so will not bring about a change in the end point.

Procedure (continued)

- The titration is stopped when the colour of the indicator changes from yellow to red (pink).
- The volume of acid added is noted. Two further **accurate** titrations are carried out. The hydrochloric acid solution is added drop by drop as the end point is approached.
- At the end point, one drop of acid turns the solution in the conical flask a faint red (pink) colour.
- The results of these two accurate titrations should agree to within 0.1 cm^3. If they do not agree, a further titration must be carried out until agreement to within 0.1 cm^3 is obtained.
- The titration result (also called the **titre**) for the experiment is taken as the average of the two readings which agree to within 0.1 cm^3.

Explanation

- The indicator changes from yellow to red (pink) because the solution in the conical flask becomes acidic.
- The rough titration reading is an indication of the approximate end point. It gives you an idea of where the accurate end point is located, i.e. it helps you to locate the accurate end point more precisely. It also saves time as it allows rapid addition from the burette until the end point is close rather than adding the solution drop-by-drop during the entire titration.
- In calculations, the rough titration figure should be neglected. For example, if the three titration readings are 22.9 cm^3, 22.4 cm^3 and 22.5 cm^3, the titration figure to be used in calculations is the average of 22.4 and 22.5, i.e. 22.45 cm^3.

Calculations

The method of calculating the concentration of the hydrochloric acid solution is shown in Example 12.19 in the next section.

DIGITAL: A video of this experiment is available on FolensHIVE.

12.11 Solving volumetric problems: Calculating the concentration of a solution of unknown concentration from titration data

The most common type of problem encountered in volumetric analysis is where we are required to find the concentration of a solution of a given substance. For example, in Experiment 12.3 we need to work out the concentration of the hydrochloric acid solution. The type of calculation involved is shown in the following examples.

Example 12.19

Question

1.45 g of sodium carbonate were dissolved in water and the solution was made up to 250 cm^3 in a volumetric flask. 25 cm^3 of this solution were titrated against a solution of hydrochloric acid using methyl orange as indicator. One rough and two accurate titrations were performed. The titration results are shown in the following table.

Titration	1	2	3
Volume (cm^3)	19.8	19.5	19.6

The equation for the reaction is: $Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

Calculate the concentration of the hydrochloric acid solution in (a) moles per litre and (b) grams per litre. (H = 1, C = 12, 0 = 16, Na = 23, Cl = 35.5)

Answer

Step 1

Calculate the molarity of the sodium carbonate solution. We can calculate it from first principles as follows:

1 mole Na_2CO_3 in 1 litre of solution $\rightarrow$ 1M Na_2CO_3 solution

i.e. 106 g Na_2CO_3 in 1 litre of solution $\rightarrow$ 1 M Na_2CO_3 solution

1 g Na_2CO_3 in 1 litre of solution $\rightarrow \frac{1}{106}$ M Na_2CO_3 solution

1.45 g Na_2CO_3 in 1 litre of solution $\rightarrow \frac{1 \times 1.45}{106}$ M Na_2CO_3 solution

1.45 g Na_2CO_3 in 250 cm^3 of solution $\rightarrow \frac{4 \times 1.45}{106}$ M Na_2CO_3 solution

$= 0.055$ M Na_2CO_3 solution

Step 2

Use the concentration of the sodium carbonate solution to calculate the concentration of the hydrochloric acid solution.

To do this, we will first deduce a general expression for answering this type of question. Consider the reaction between sodium carbonate and hydrochloric acid:

$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$

From the balanced equation, we see that two moles of acid react with one mole of base, i.e. the ratio of the number of moles of acid to the number of moles of base is 2 : 1.

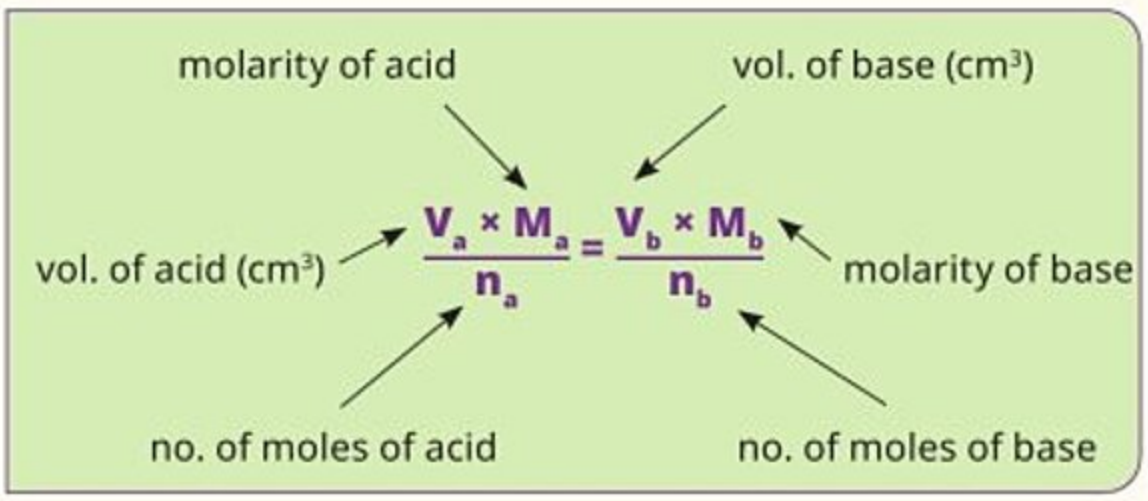
$$\frac{\text{number of moles of acid}}{\text{number of moles of base}} = \frac{2}{1}$$

If, in a given titration, V_a is the volume of acid, M_a is the molarity of the acid, n_a is the number of moles of acid, V_b is the volume of base, M_b is the molarity of the base and n_b is the number of moles of base, then the above expression becomes:

$$\frac{\frac{V_a \times M_a}{1000}}{\frac{V_b \times M_b}{1000}} = \frac{n_a}{n_b} \qquad \text{i.e. } \frac{V_a \times M_a}{V_b \times M_b} = \frac{n_a}{n_b}$$

Rearranging this expression gives:

This is a very important relationship that is very useful for solving many volumetric problems. We now substitute into this equation the values for the particular problem we are solving.


molarity of acid
vol. of base (cm³)
vol. of acid (cm³)
$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$
molarity of base
no. of moles of acid
no. of moles of base

HCl Na_2CO_3

Given:
$V_a = 19.55$*
$M_a = ?$
$n_a = 2$
$V_b = 25$
$M_b = 0.055$
$n_b = 1$

$$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

$$\frac{19.55 \times M_a}{2} = \frac{25 \times 0.055}{1}$$

$$M_a = \frac{25 \times 0.055 \times 2}{1 \times 19.55}$$

*The average of 19.5 and 19.6.

= 0.141 moles per litre.
= 0.141 × 36.5 grams per litre (M_r HCl = 36.5)
= 5.147 g/L.

Answer: Concentration of HCl solution is
(a) 0.141 moles per litre, (b) 5.147 grams per litre.

Example 12.20

Question

Hydrochloric acid and sodium hydroxide react according to the equation: $HCl + NaOH \rightarrow NaCl + H_2O$

25 cm³ of a sodium hydroxide solution were titrated against a 0.2 M HCl solution. The average titration figure was 23.5 cm³. Calculate the concentration of the sodium hydroxide solution in (a) moles per litre and (b) grams per litre. (H = 1, O = 16, Na = 23)

Answer

From the balanced equation, we see that one mole of acid reacts with one mole of base, i.e. $n_a = 1$ and $n_b = 1$.

HCl NaOH

Given:
$V_a = 23.5$
$M_a = 0.2$
$n_a = 1$
$V_b = 25$
$M_b = ?$
$n_b = 1$

$$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

$$\frac{23.5 \times 0.2}{1} = \frac{25 \times M_b}{1}$$

$$M_b = \frac{23.5 \times 0.2}{25}$$

= 0.188 moles per litre.
= 0.188 × 40 grams per litre (M_r NaOH = 40)
= 7.52 g/L.

Answer: Concentration of NaOH solution is
(a) 0.188 M, (b) 7.52 g/L.

TEST YOURSELF: Attempt Questions 12.7–12.8 and W12.12–W12.14.

12.4 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 8 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 8

To make up an approximate 0.1 M solution of sodium hydroxide and to standardise it (i.e. obtain its exact concentration) with a standard hydrochloric acid solution

Introduction

Since sodium hydroxide is deliquescent (i.e. it absorbs so much water vapour from the air that it becomes a solution), we cannot weigh out a fixed amount of it and make up a solution of exact concentration. In this experiment, we will make up an approximate 0.1 M solution of sodium hydroxide and standardise it by titrating it against a hydrochloric acid solution of known concentration. The equation for the reaction is:

$HCl + NaOH \rightarrow NaCl + H_2O$

Key steps in procedure

- Sodium hydroxide (about 1 g) is dissolved in deionised water and the solution is made up to 250 cm^3 in a volumetric flask following the procedure already discussed. **CAUTION!** Do not allow the sodium hydroxide to come in contact with the skin or eyes as it causes severe burns!
- The flask is inverted 20 times.
- A pipette is rinsed with deionised water followed with some of the sodium hydroxide solution.
- A burette is rinsed out with deionised water followed by some of the hydrochloric acid solution.
- A volume of 25 cm^3 of the sodium hydroxide solution is pipetted into a conical flask that has been previously rinsed with deionised water.
- A few drops of methyl orange indicator are added to the sodium hydroxide solution in the conical flask.
- The burette is filled with the dilute hydrochloric solution, the bottom of the meniscus is adjusted to the zero graduation mark, and the apparatus is set up for titration, Figure 12.16.
- A white tile is placed on the base of the retort stand and the sodium hydroxide solution is titrated against the standard solution of hydrochloric acid. One rough and two accurate titrations agreeing to within 0.1 cm^3 are carried out.

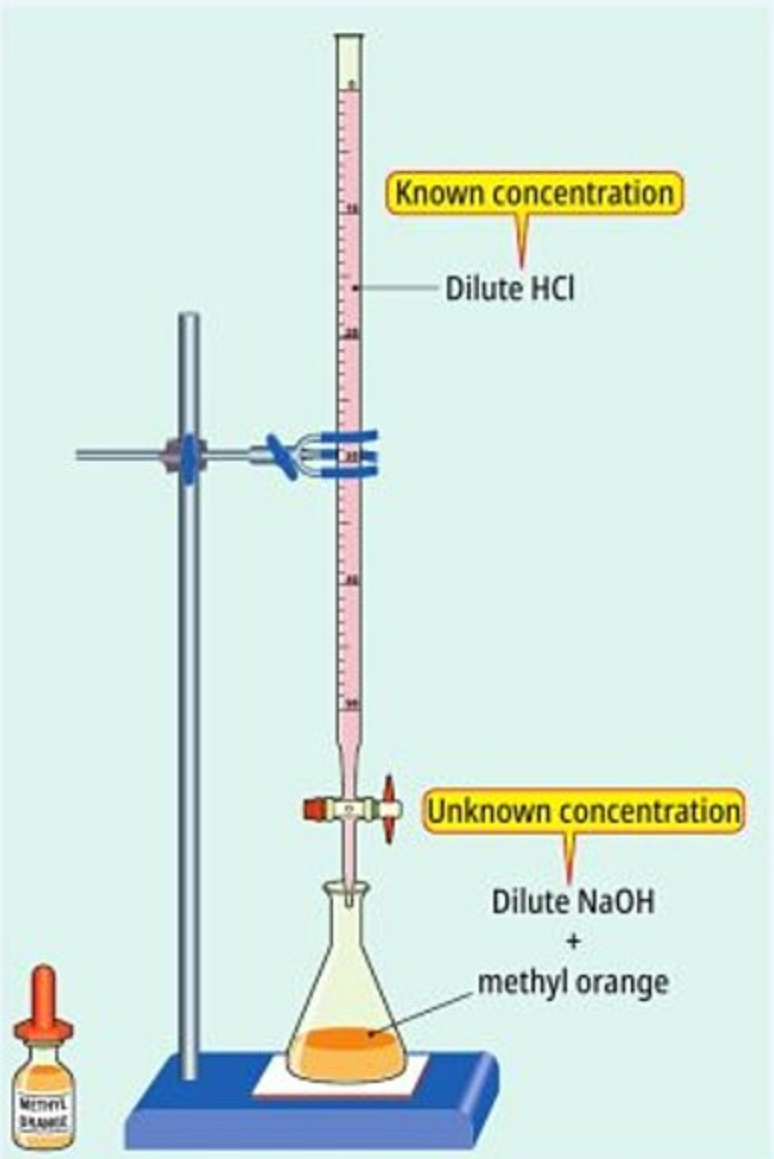


Figure 12.16

Observation

- The methyl orange indicator changes from yellow to red (pink).

Explanation

- The methyl orange changes colour from yellow to red (pink) because the solution in the conical flask becomes acidic.

DIGITAL: A video of this experiment is available on FolensHIVE.

Calculations

- From the results of your titration, work out the exact concentration of the sodium hydroxide solution. Express the concentration of the sodium hydroxide solution (a) in moles per litre and (b) in grams per litre. A sample calculation has been given in Example 12.20.

12.5 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 9 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 9

To determine the concentration of a solution of ammonia using a standardised HCl solution (strong acid–weak base titration)

Introduction

In Experiment 12.3, we used a standard solution of sodium carbonate to determine the exact concentration of a hydrochloric acid solution. This hydrochloric acid solution may now be used to standardise (find the exact concentration of) other solutions, e.g. a solution of ammonia. Ammonia is supplied to laboratories as a highly concentrated solution of ammonia (usually about 16 M NH_3). Therefore, your teacher will supply you with a more dilute solution of ammonia to use.

The equation for the reaction is:

$$HCl_{(aq)} + NH_{3(aq)} \rightarrow NH_4Cl_{(aq)}$$

Recall that the 'aq' (aqueous) indicates that everything is dissolved in solution. A solution of ammonia in water is also called ammonium hydroxide as NH_4^+ ions and OH^- ions (from water) are present in solution.

Key steps in procedure

- A pipette is rinsed with deionised water and with some of the ammonia solution.
- A burette is rinsed out with deionised water and with some of the hydrochloric acid solution.
- A volume of 25 cm^3 of the ammonia solution is pipetted into a conical flask that has been previously rinsed with deionised water.
- A few drops of methyl orange indicator are added to the ammonia solution in the conical flask.
- The burette is filled with the dilute hydrochloric solution, the bottom of the meniscus is adjusted to the zero graduation mark, and the apparatus is set up for titration, Figure 12.17.
- A white tile is placed on the base of the retort stand and the ammonia solution is titrated against the standard solution of hydrochloric acid. One rough and two accurate titrations agreeing to within 0.1 cm^3 are carried out.

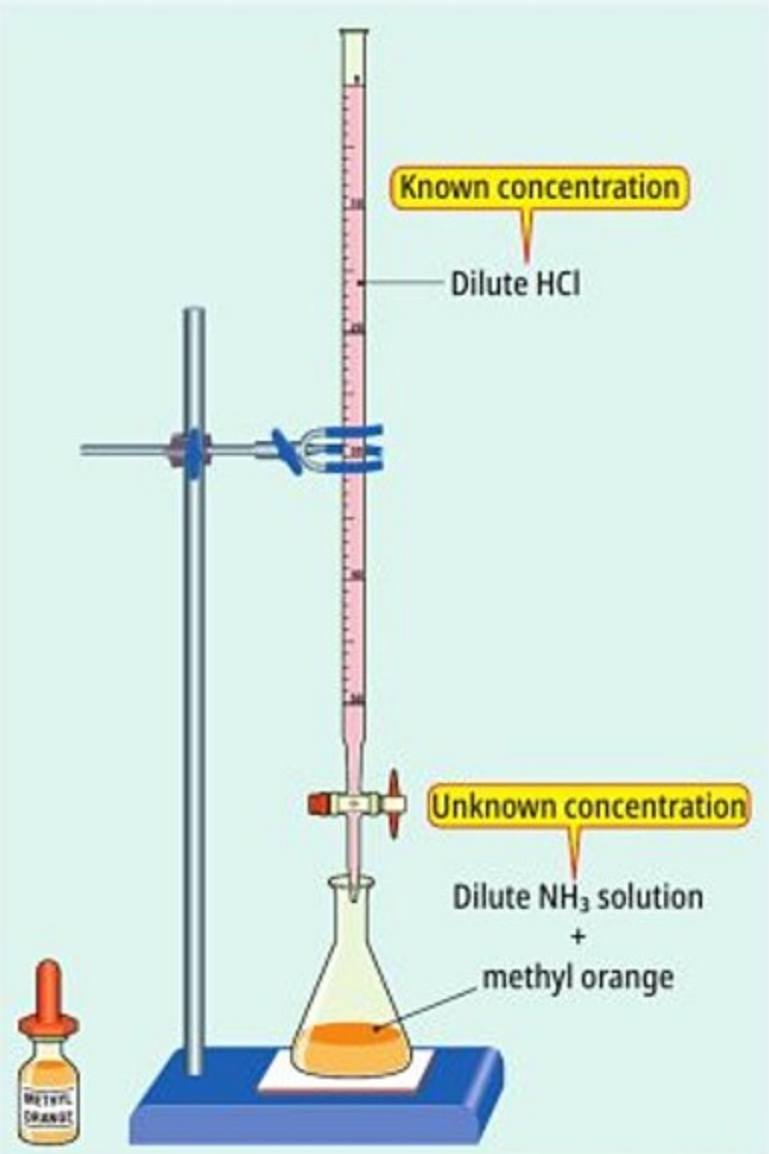


Figure 12.17

Observation

- The methyl orange indicator changes from yellow to red (pink).

Explanation

- The methyl orange changes colour from yellow to red (pink) because the solution in the conical flask becomes acidic.

Calculations

- From the results of your titration, work out the exact concentration of the ammonia solution. Express the concentration of the ammonia solution (a) in moles per litre and (b) in grams per litre. A sample calculation is given in Example 12.22.

Example 12.22

Question

Hydrochloric acid and ammonia solution react according to the equation:

$HCl + NH_3 \rightarrow NH_4Cl$

25 cm^3 of an ammonia solution were titrated against a 0.15 M HCl solution. The average titration figure was 22.5 cm^3. Calculate the concentration of the ammonia solution in (a) moles per litre and (b) grams per litre. (H = 1, N = 14)

Answer

From the balanced equation, we see that one mole of acid reacts with one mole of base, i.e. $n_a = 1$ and $n_b = 1$.

HCl NH_3

Given:

$V_a = 22.5$

$M_a = 0.15$

$n_a = 1$

$V_b = 25$

$M_b = ?$

$n_b = 1$

$$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

$$\frac{22.5 \times 0.15}{1} = \frac{25 \times M_b}{1}$$

$$M_b = \frac{22.5 \times 0.15}{25}$$

= 0.135 moles per litre.

= 0.135 × 17 grams per litre (M_r NH_3 = 17)

= 2.295 g/L.

Answer: Concentration of NH_3 solution is (a) 0.135 M, (b) 2.295 g/L.

12.6 Experiment

Full step-by-step details of the procedure for carrying out this experiment are given in Experiment 10 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 10

To determine the concentration of ethanoic acid (acetic acid) in vinegar (weak acid–strong base titration)

Introduction

Vinegar is a dilute solution of an acid called ethanoic acid, CH_3COOH, the old name of which is acetic acid. The amount of ethanoic acid in vinegar can be determined by titrating the vinegar against a standard sodium hydroxide solution. The equation for the reaction is:

CH_3COOH	+	$NaOH$	→	CH_3COONa	+	H_2O
ethanoic acid		sodium hydroxide		sodium ethanoate		

To detect the end point, we use an indicator called phenolphthalein. Phenolphthalein is colourless in an acid and pink in a base. (Phenolphthalein is suitable because we are titrating a weak acid against a strong base. This will be explained in more detail in Chapter 19.)

As the concentration of the sodium hydroxide solution being used is quite small (0.1 M approx.), it is necessary to dilute the vinegar to avoid having to use a large volume of sodium hydroxide solution to neutralise it. Alternatively you could say that, since the vinegar is much more concentrated than the sodium hydroxide solution, a very small amount of vinegar would be needed to neutralise the base and this would be likely to contribute to a higher percentage error in the experiment.

Key steps in procedure

- Two 25 cm^3 samples of vinegar are added to a 250 cm^3 volumetric flask, Figure 12.18. Deionised water is added until the bottom of the meniscus is level with the graduation mark. Note that the sample of vinegar has been diluted by a factor of five (from 50 cm^3 to 250 cm^3) in the volumetric flask.
- The pipette is washed with deionised water and with the standard sodium hydroxide solution.
- Use the pipette to transfer 25 cm^3 of the standard sodium hydroxide solution to a conical flask that has been previously rinsed with deionised water.
- About three drops of phenolphthalein indicator are added to the sodium hydroxide solution in the conical flask.

Observation

- The phenolphthalein is a pink colour in the sodium hydroxide solution.

Explanation

- Phenolphthalein indicator is pink in a basic (alkaline) solution.

Procedure (continued)

- The burette is rinsed with water and with some of the diluted vinegar.
- Using a small funnel, the burette is filled with the diluted vinegar. The funnel is removed and the bottom of the meniscus adjusted to the zero graduation mark. A white tile is placed on the base of the retort stand, Figure 12.19.
- The diluted vinegar is titrated against the sodium hydroxide solution. One rough and two accurate titrations, agreeing to within 0.1 cm^3, are carried out.

Observation

- At the end point, the phenolphthalein changes from pink to colourless.

Calculations

- From the results of the titration, work out the concentration of ethanoic acid in the original vinegar (a) in moles per litre, (b) in grams per litre and (c) in % w/v. A sample calculation is given in Example 12.23.

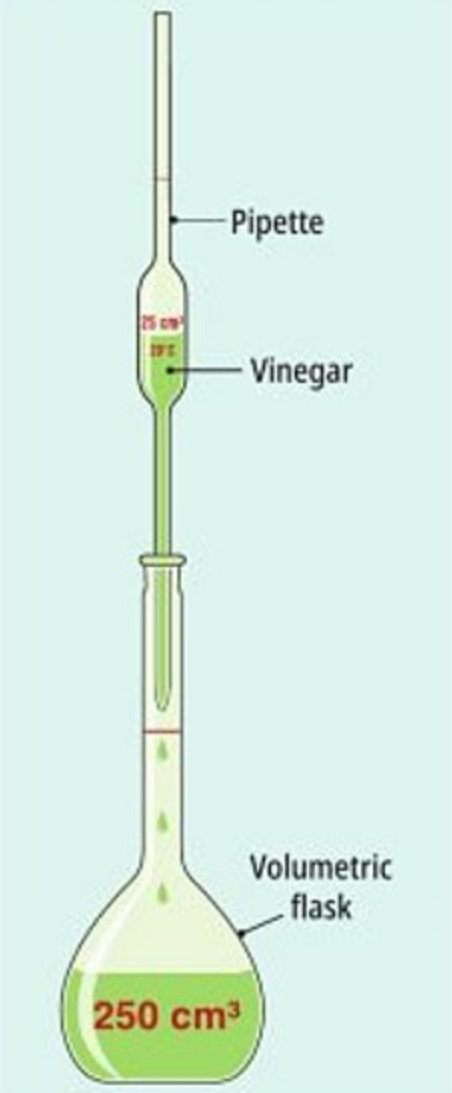


Figure 12.18 The vinegar is diluted by a factor of five by pipetting two 25 cm^3 samples of vinegar into a 250 cm^3 volumetric flask and making the solution up to the graduation mark with deionised water

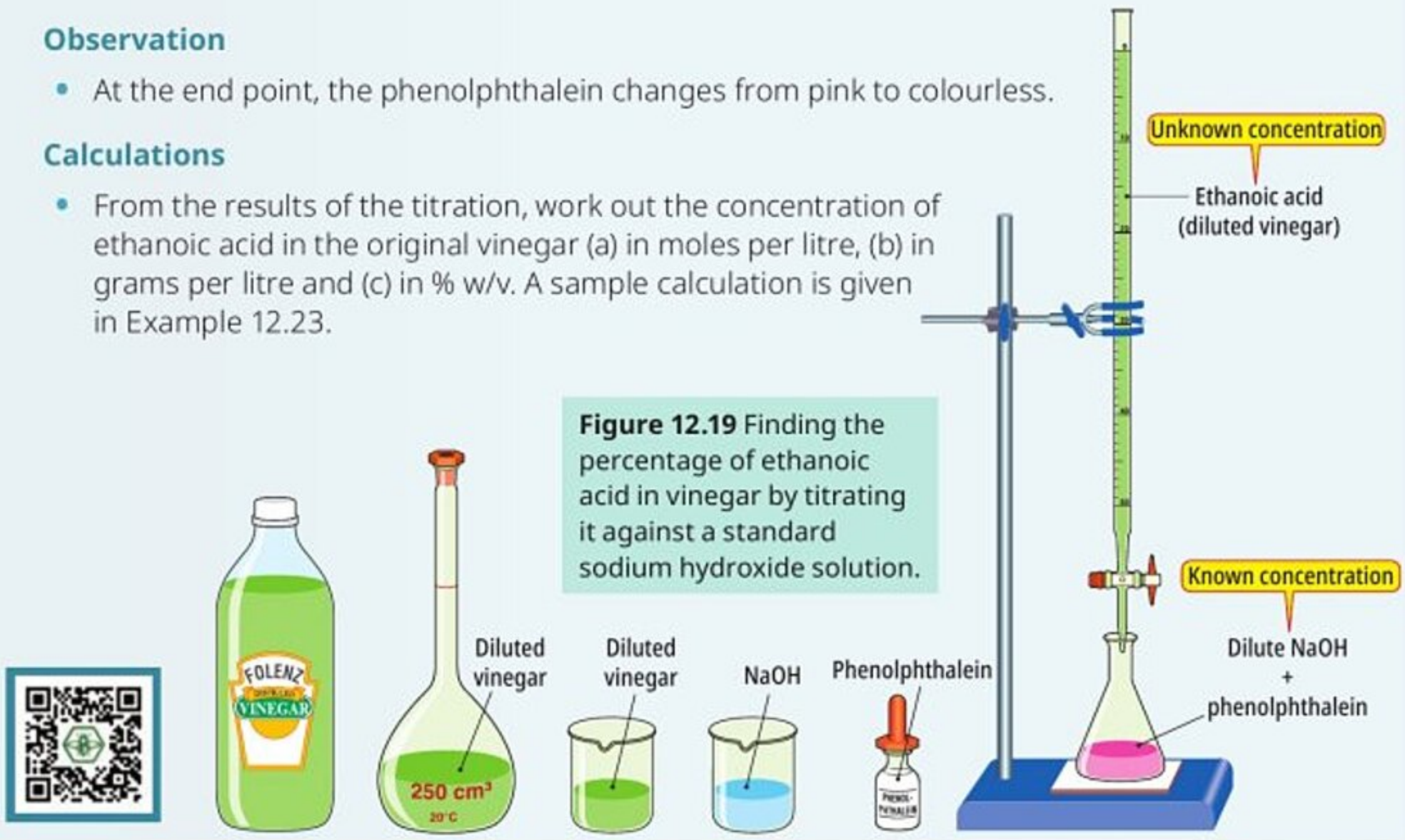


Figure 12.19 Finding the percentage of ethanoic acid in vinegar by titrating it against a standard sodium hydroxide solution.

Note: In the experiment, it is best to use colourless vinegar. The green colour is used in Figure 12.26 to distinguish the vinegar from the sodium hydroxide solution (blue) and the colour of the sodium hydroxide and phenolphthalein in the conical flask (pink). The important colour change to remember is the colour change at the end point, i.e. pink to colourless.

Example 12.23

Question

A 20 cm^3 sample of vinegar was diluted to 100 cm^3 in a volumetric flask. This diluted solution was then titrated against 20 cm^3 of 0.12 M NaOH solution. The balanced equation for the reaction is:

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$

The average titration figure was 14.2 cm^3. Calculate the concentration of ethanoic acid in the original vinegar in (a) mol/L, (b) g/L and (c) % w/v. (H = 1, C = 12, O = 16)

Answer

Step 1

Calculate concentration of ethanoic acid in diluted solution.

From the balanced equation, we see that one mole of acid reacts with one mole of base, i.e. $n_a = 1$ and $n_b = 1$.

CH_3COOH $NaOH$

Given:

$V_a = 14.2$

$M_a = ?$

$n_a = 1$

$V_b = 20$

$M_b = 0.12$

$n_b = 1$

$$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

$$\frac{14.2 \times M_a}{1} = \frac{20 \times 0.12}{1}$$

$$M_a = \frac{20 \times 0.2}{14.2}$$

$= 0.169$ moles per litre.

Step 1

Calculate concentation of ethanoic acid in original vinegar.

Since the solution was diluted by a factor of five, concentration of ethanoic acid in original vinegar

$= 0.169 \times 5$ moles per litre

$= 0.845$ mol/L (a)

$= 0.845 \times 60$ g/L (M_r $CH_3COOH = 60$)

$= 50.7$ g/L (b)

Since there are 50.7 g of ethanoic acid in a litre of vinegar, there are 5.07 g of ethanoic acid in 100 cm^3 of vinegar.

Therefore, % w/v = 5.07% (c)

Answer: Concentration of ethanoic acid in vinegar is (a) 0.845 M (b) 50.7 g/L (c) 5.07% w/v.

TEST YOURSELF: Attempt Questions W12.15–W12.27.

Summary What I should know

- The concentration of a solution is the amount of solute that is dissolved in a given volume of solution. Concentration may be expressed in terms of percentage of solute or in parts per million or in moles per litre (molarity).
- A 1 M solution is one that contains one mole of the solute dissolved in one litre of solution.
- Serial dilution is a step-by-step dilution process where a solution is diluted multiple times in a systematic way
- To calculate the number of moles, when the volume and the molarity of the solution are given, use the formula:

  $$\text{number of moles} = \frac{\text{volume}^* \times \text{molarity}}{1000} \qquad (*\text{in cm}^3)$$

- For calculations involving dilution of solutions, use the formula:

  $$\frac{\text{Vol}_{dil}^* \times \text{M}_{dil}}{1000} = \frac{\text{Vol}_{conc}^* \times \text{M}_{conc}}{1000} \qquad (*\text{in cm}^3)$$

- A standard solution is a solution of precisely known concentration.
- A primary standard is a substance that can be obtained in a stable, pure and soluble solid form so that it can be weighed out and dissolved in water to give a solution of accurately known concentration.
- A titration is a laboratory procedure where a measured volume of one solution is added to a known volume of another solution until the reaction is complete.
- Many volumetric problems may be solved using the formula:

  $$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

- The **analyte** is the chemical species being analysed to determine its concentration, identity or properties.
- Titration data may be used to calculate the unknown concentration of a solution.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain how concentrations of solutions are expressed.			
Convert between units of concentration.			
Calculate the number of moles given a volume and molarity of a solution.			
Explain the concepts of standard solutions and primary standards.			
Perform calculations involving data from simple dilutions and serial dilutions.			
Determine the concentration of analytes by titration using primary standard solutions or solutions standardised using primary standards.			

Chapter review questions

When answering these questions, use the following values of relative atomic masses:
H = 1, He = 4, Li = 7, C = 12, N = 14, O =16, F = 19, Na = 23, Mg = 24, Al = 27, Si = 28, P = 31, S = 32, Cl = 35.5, K = 39, Ca = 40, Cr = 52, Fe = 56, Cu = 63.5, Zn = 65, Br = 80, Ag = 108, Sn = 119, I = 127, Pb = 207.

Concentrations of solutions

12.1 A sample of sea water has a mass of 1.3 kg. On evaporating the water, 148 g of salt were recovered from it. Express the concentration of the salt as % w/w.

12.2 Convert the following concentrations to ppm:

(a) 0.75 g/L
(b) 0.06 g/L
(c) 0.017 g/100 cm^3
(d) 0.0003 g/100 cm^3.

12.3 Calculate the concentration in grams per litre of:

(a) 1 M NaOH
(b) 2 mol/L KOH
(c) 0.125 MH_2SO_4
(d) 0.01 mol/L Na_2CO_3
(e) 0.005 mol/L HNO_3.

12.4 Calculate the number of moles of sulfuric acid in:

(a) 25 cm^3 of 0.01 M H_2SO_4
(b) 18 cm^3 of 2.5 M H_2SO_4
(c) 8.7 cm^3 of 0.5 M H_2SO_4

Reaction between a solution and a solid

12.5 Iron reacts with dilute sulfuric acid according to the equation:

$Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$

What mass of iron will react with 75 cm^3 of 0.5 M H_2SO_4?

Dilution of solutions

12.6 **(a)** Distinguish between the terms *simple dilution* and *serial dilution*.

(b) With the aid of a labelled diagram, describe how you would carry out a four-step serial dilution of a solution of 0.5 M sodium chloride using a dilution factor of 1:10.

(c) State the concentration of each solution at the end of the experiment.

(d) Why is it necessary to use a clean graduated dropper at each stage of the dilution process?

Titrations: Volumetric problems

12.7 With regard to the procedure for carrying out a titration, answer the following questions.

(a) Why is the tap of the burette opened briefly before the titration is begun?

(b) Why is it necessary to remove the funnel from the burette before the titration is begun?

(c) What is the purpose of placing the conical flask on a white tile?

(d) Why is a volumetric flask preferable to a graduated cylinder for making up a solution?

(e) Why is a conical flask preferable to a beaker for carrying out a titration?

(f) Which of the pieces of apparatus, the pipette, the burette or the conical flask, should not be rinsed with the solution it is to contain?

(g) What is the purpose of carrying out a rough titration?

(h) Why should the conical flask be swirled during the titration?

(i) Would any error be introduced if the conical flask contained some droplets of deionised water before the base is pipetted into it? Explain your answer.

(j) Sodium hydroxide is not normally placed in burettes. What is the reason for this?

(k) When reading the volume of liquid in a burette, what precautions should be taken to ensure that the reading is taken correctly?

(l) Why is it necessary to wash down the sides of the conical flask during a titration?

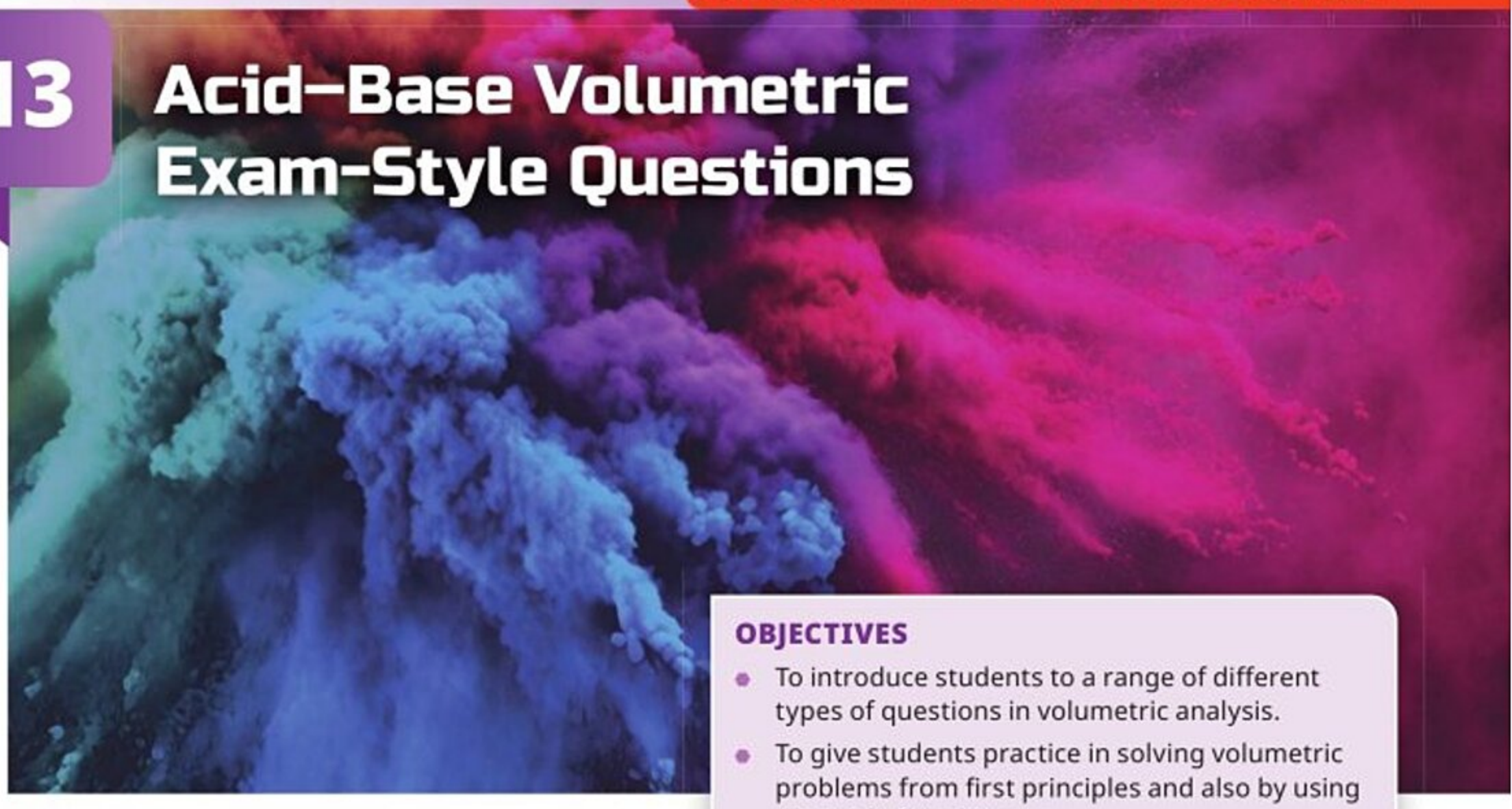
(m) Why is it not advisable to insert a pipette into a volumetric flask in order to transfer some solution directly to a conical flask?

12.8 It was found that 11.5 cm^3 of a 0.5 M sulfuric acid solution neutralised 25 cm^3 of a given solution of sodium hydroxide. The balanced equation for the reaction is:

$H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$

Calculate the concentration of the sodium hydroxide solution in (a) mol/L and (b) g/L.

13 Acid–Base Volumetric Exam-Style Questions



OBJECTIVES

- To introduce students to a range of different types of questions in volumetric analysis.
- To give students practice in solving volumetric problems from first principles and also by using some key formulas.
- To ensure that students know the importance of accuracy and precision in volumetric analysis practical work.

13.1 Introduction

In Chapter 12 we studied how many problems in volumetric analysis can be solved from first principles. Thus, in Examples 12.1–12.7 we saw how all the problems could be solved starting with some basic definitions without the need to use any formulas. We also saw how the molarity of the standard solution of sodium carbonate that was made up by you, could be calculated by starting with the basic definition of a 1 M solution. In addition, we learned in Example 12.19 that this problem could be solved using both first principles and also by means of a general formula for calculating unknown concentrations given the results of titration data, Figure 13.1.

Learning to solve problems from first principles is very helpful in giving you an understanding of key concepts in volumetric analysis. However, it can be time-consuming to do this for every volumetric problem. Therefore, in this chapter, we will introduce you to some key formulas to help you solve volumetric problems when you are under time pressure in exams. When solving a problem in an exam paper from first principles or using formulas, always remember that it is very important to show all your work.

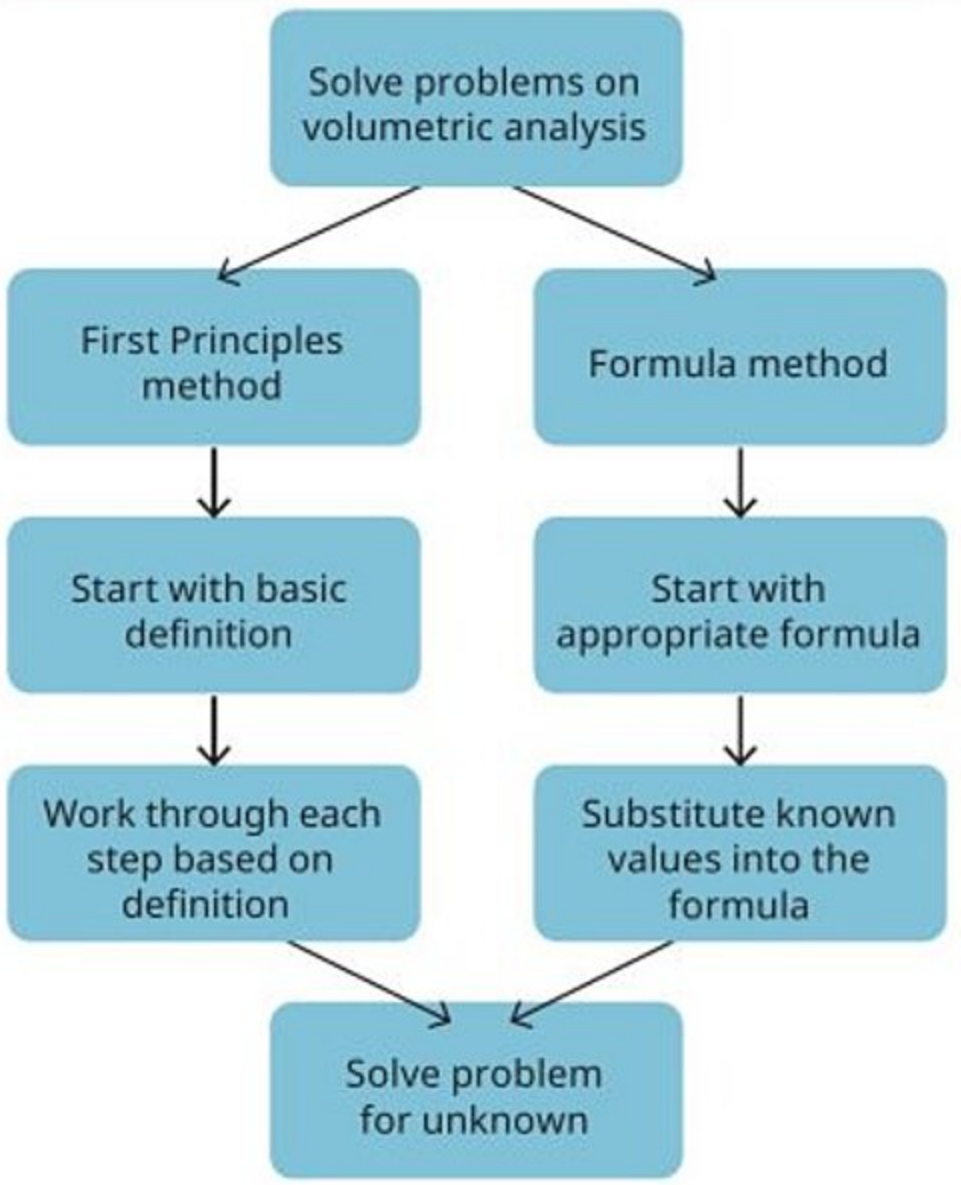

Solve problems on volumetric analysis
First Principles method
Formula method
Start with basic definition
Start with appropriate formula
Work through each step based on definition
Substitute known values into the formula
Solve problem for unknown

Figure 13.1 The first principles method of solving problems is a good starting point as it ensures that you understand what you are doing. However, in examinations the use of key formulas is faster and very effective as long as you show all your calculations.

13.2 Key formulas for solving volumetric problems

In this section, we will summarise some of the key formulas that we have met so far in stoichiometry and volumetric analysis, Table 13.1. We will then show how these key formulas can be used in solving some volumetric problems in exam-style questions.

	Formula	Comment
1.	Number of moles = $\frac{\text{Mass (in grams)}}{\text{Relative Molecular Mass}}$	This is a very useful formula (Chapter 8) for calculating the number of moles of a substance when we know the relative molecular mass. It can also be manipulated to: (i) Calculate the mass if we know the number of moles and relative molecular mass or (ii) Calculate the relative molecular mass if we know the mass and number of moles.
2.	Number of moles = $\frac{\text{volume}^* \times \text{molarity}}{1000}$ (*in cm^3)	This is a very useful formula (Chapter 12) for calculating the number of moles when given a volume of solution and the molarity of the solution.
3.	$\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$	This is a very useful formula (Chapter 12) for calculating the unknown concentration of a solution from titration data.
4.	Density = $\frac{\text{Mass}}{\text{Volume}}$	You have met this formula when studying Junior Cycle science. It is very useful if we are given the density of a liquid and its volume and we need to calculate the mass of the liquid.

Table 13.1 Some key formulas in volumetric analysis

13.3 Solving exam-style problems

We will now study some examples of exam-style questions to show you how the above formulas can be used. So far, we have been using values of relative atomic masses which have been rounded off. This was done to enable you to concentrate on acquiring basic skills of calculations without being distracted by consulting the *Formulae and Tables* booklet of the SEC every time you wished to find out the exact relative atomic mass of an element.

However, in keeping with the style of sample exam papers published by the State Examinations Commission, instead of rounding off relative atomic masses, we will now use the values given in the SEC booklet.

The relative atomic masses most commonly encountered in acid–base volumetric analysis are given in Table 13.2.

Element	Relative atomic mass
H	1.008
C	12.01
N	14.01
O	16.00
Na	22.99
Mg	24.31
S	32.07
Cl	35.45

Table 13.2 Relative atomic masses of elements commonly encountered in acid–base volumetric problems

Example 13.1

Question

To determine the concentration of ethanoic acid in a sample of vinegar, Figure 13.2, 25.0 cm^3 of the vinegar were diluted to 250 cm^3 and then the diluted vinegar was titrated with a previously standardised solution which contained 1.20 g of sodium hydroxide in 500 cm^3 of solution.

On average, 18.75 cm^3 of the diluted vinegar were required to neutralise 25.0 cm^3 of this sodium hydroxide solution.

The equation for the titration reaction is:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

(a) Calculate:

(i) the number of moles of sodium hydroxide in each 25.0 cm^3 portion

(ii) the number of moles of ethanoic acid per cm^3 of *diluted* vinegar.

(b) Find the concentration of ethanoic acid in the original vinegar:

(i) in terms of moles per litre.

(ii) as a percentage (w/v).

(Given H = 1.008, C = 12.01, O = 16, Na = 22.99) [LCH]

Figure 13.2 Vinegar contains an acid called ethanoic acid (acetic acid).

Answer

(a) (i) First calculate the molarity of 1.2 g sodium hydroxide solution in 500 cm^3 solution.
We can do this using first principles or using the formula.

Step 1

Calculate the molarity of the NaOH solution.

Relative molecular mass NaOH = 22.99 + 16 + 1.008 = 39.998

$$\text{Using formula 1, no. of moles NaOH} = \frac{\text{Mass}}{\text{Relative Molecular Mass}} = \frac{1.20}{39.998} = 0.03 \text{ moles}$$

0.03 mole of NaOH in 500 cm^3 solution = 0.06 mole NaOH/L = 0.06 M solution

Step 2

Calculate the number of moles of NaOH in 25 cm^3 of the 0.06 M solution.

$$\text{Using formula 2, no. of moles NaOH} = \frac{\text{volume} \times \text{molarity}}{1000} = \frac{25 \times 0.06}{1000} = 0.0015 \text{ moles}$$

Answer: There is 0.0015 mole NaOH in each 25 cm^3 portion.

(a) (ii) Calculate the number of moles of ethanoic acid per cm^3 of *diluted* vinegar.

Step 1

Calculate the molarity of the diluted ethanoic acid (vinegar) solution.

CH_3COOH $NaOH$

$$\text{Using formula 3: } \frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$$

Given

$V_a = 18.75$	$V_b = 25$
$M_a = ?$	$M_b = 0.06$
$n_a = 1$	$n_b = 1$

Step 2

Substitute in the values: $\frac{18.75 \times M_a}{1} = \frac{25 \times 0.06}{1}$

Step 3

Solve for the unknown (molarity of acid):

$$M_a = \frac{25 \times 0.06}{18.75} = 0.08 \text{ mole/L (diluted vinegar)}$$

Step 4

Calculate the number of moles of ethanoic acid per cm^3 of diluted vinegar.

From Step 3 above, we see that there is 0.08 mole in one litre (1000 cm^3) of solution.

Therefore, there are $\frac{0.08}{1000} = 0.0008$ mole per cm^3 of diluted vinegar.

Answer: Number of moles of ethanoic acid per cm^3 of diluted vinegar = 0.0008

(b) (i) Find the concentration of ethanoic acid in the original vinegar in terms of moles per litre.

Concentration of ethanoic acid in diluted vinegar = 0.08 M

Since 25 cm^3 of the vinegar were diluted to 250 cm^3, dilution factor = 10

Therefore, concentration of ethanoic acid in original vinegar = 0.08 × 10 = 0.8 M

Answer: Concentration of ethanoic acid in original vinegar is 0.8 M

(b) (ii) Find the concentration of ethanoic acid in the original vinegar as a percentage (w/v)

Step 1

Calculate the relative molecular mass of CH_3COOH as follows:

C = 2 × 12.01 = 24.02
O = 2 × 16 = 32
H = 4 × 1.008 = 4.032
M_r = 60.052

Step 2

Convert molarity of CH_3COOH to grams per litre:

A 1 M solution of CH_3COOH contains 60.052 g/L

A 0.8 M solution of CH_3COOH contains 60.052 × 0.8 g/L = 48.0416 g/L

Step 3

Convert grams per litre to w/v.

48.0416 g/L = 4.80416 g/100 cm^3 = 4.80% w/v

Answer: Concentration of ethanoic acid in original vinegar = 4.80% w/v

Example 13.2

Question

A student carried out an experiment to determine the concentration of ethanoic acid in vinegar, Figure 13.3. A 10.0 cm^3 portion of the vinegar was first diluted to exactly 50.0 cm^3. The diluted vinegar solution was titrated against a 0.09 M sodium hydroxide solution in a conical flask. On average, 12.4 cm^3 of the *diluted* vinegar were required to neutralise 25.0 cm^3 of the NaOH solution.

The titration reaction is described by the following balanced chemical equation:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

[LCH]

Figure 13.3 Many brands of vinegar state the % ethanoic acid (acetic acid) in the vinegar. Table vinegar usually contains 4–6% ethanoic acid.

Question

(a) (i) Name the piece of apparatus used to measure accurately the 10.0 cm^3 portion of the original vinegar.

Answer

A pipette is used (or a burette is also acceptable).

Question

(ii) Describe how this piece of apparatus was rinsed before use.

Answer

The pipette is first rinsed with deionised water and then with the solution (vinegar) that it is to contain.

Question

(iii) Describe a suitable method to dilute the 10.0 cm^3 portion of the original vinegar to exactly 50.0 cm^3.

Answer

1. Using a pipette place 10 cm^3 of vinegar in a 50 cm^3 volumetric flask.
2. Add deionised water.
3. Ensure that the bottom of the meniscus is level with the graduation mark.

Question

(b) (i) Calculate the volume of *undiluted* vinegar which would be required to neutralise 25.0 cm^3 of the 0.09 M NaOH solution.

Answer

Step 1

Note that 10 cm^3 vinegar were diluted to 50 cm^3. Therefore, the dilution factor = 5.

Step 2

We are told in the question that 12.4 cm^3 of the *diluted* vinegar neutralised 25.0 cm^3 of the NaOH solution.

Step 3

Therefore, only $\frac{12.4}{5}$ = 2.48 cm^3 of the *undiluted* vinegar would be required to neutralise 25.0 cm^3 of the 0.09 M NaOH solution.

Question

(ii) Outline an advantage of diluting the vinegar before carrying out the titration.

Answer

If the vinegar was not diluted, a much smaller volume of this more concentrated solution of ethanoic acid would be required to neutralise the dilute sodium hydroxide solution. (This small volume was calculated in (b)(i) above as only 2.48 cm^3.) Smaller volumes have a higher percentage error, because even a slight misreading of the volume will have a greater impact on the accuracy of the results. Diluting the vinegar increases the volume needed for neutralisation, which in turn **makes the percentage error smaller**, leading to a more accurate titration figure. (We will be discussing errors in volumetric analysis in more detail in Chapter 16.)

- Another acceptable answer was that the dilute solution of ethanoic acid means that a less concentrated solution of NaOH can be used to neutralise it. Since NaOH is a caustic substance, it is safer to use a less concentrated solution.

EXAM TIP!

Key words to use when explaining about the dilution of the vinegar are **smaller percentage error.**

Question

(c) (i) Name a suitable indicator for this titration.

Answer

Phenolphthalein.

Question

(ii) State the colour change observed at the end point.

EXAM TIP!

When asked for a colour change, you must always state **two** colours and make it obvious what colour was present at the beginning and at the end. Also, the word 'clear' is not acceptable as a colour.

Answer

The colour of the phenolphthalein change is **from pink to colourless.**

Question

(d) (i) Calculate the number of moles of sodium hydroxide in each 25.0 cm^3 portion.

Answer

Step 1

To calculate the number of moles of sodium hydroxide in each 25.0 cm^3 portion, use formula No. 2.

Step 2

Input the information into the formula and solve:

$$\text{No. of moles NaOH} = \frac{\text{volume} \times \text{molarity}}{1000} = \frac{25 \times 0.09}{1000} = 0.00225 \text{ mole}$$

Answer: There are 0.00225 mole NaOH in each 25 cm^3 portion.

Question

(ii) Calculate the number of moles of ethanoic acid in each cm^3 of the *diluted* vinegar.

Answer

Note from the question that 12.4 cm^3 of the diluted vinegar were required to neutralise 25.0 cm^3 of the NaOH solution. Since CH_3COOH and NaOH react in the ratio of 1:1, this means that the 12.4 cm^3 of the diluted vinegar must also contain 0.00225 mole ethanoic acid.

12.4 cm^3 contain 0.00225 moles ethanoic acid

1 cm^3 contains $\frac{0.00225}{12.4} = 0.00018$ moles

Question

(iii) Calculate the concentration of ethanoic acid in the original vinegar in moles per litre.

Answer

Step 1

Calculate the molarity of the diluted ethanoic acid (vinegar) solution.

CH_3COOH	NaOH
$V_a \times M_a$	$V_b \times M_b$

Using formula 3: $\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$

Given

$V_a = 12.4$	$V_b = 25$
$M_a = ?$	$M_b = 0.096$
$n_a = 1$	$n_b = 1$

Step 2

Substitute in the values $\frac{12.4 \times M_a}{1} = \frac{25 \times 0.09}{1}$

Step 3

Solve for the unknown (molarity of acid):

$$Ma = \frac{25 \times 0.09}{12.4} = 0.1815 \text{ mole/L}$$

You could also answer this question from part **(ii)** using first principles rather than using the above equation:

In part **(ii)** we calculated that in 1 cm^3 there is 0.00018 mol ethanoic acid.

Therefore, in 1000 cm^3 there is 0.00018 × 1000 = 0.18 mole/L.

Step 4

Since the original vinegar was diluted 5 times:

- Concentration of ethanoic acid in original vinegar = 0.1815 × 5 = 0.91M.

Question

(iv) Calculate the concentration of ethanoic acid in the original vinegar in % (w/v).

Answer

Step 1

Calculate the relative molecular mass of CH_3COOH as follows:

C = 2 × 12.01 = 24.02

O = 2 × 16 = 32

H = 4 × 1.008 = 4.032

M_r = 60.052

Step 2

Convert molarity of CH_3COOH to grams per litre:

A 1 M solution of CH_3COOH contains 60.052 g/L

A 0.91 M solution of CH_3COOH contains 60.052 × 0.91 g/L = 54.65 g/L

Step 3

Convert grams per litre to w/v

54.65 g/L = 5.465 g/100 cm^3 = 5.465%

Answer: Concentration of ethanoic acid in original vinegar = 5.465% w/v

» Study Example 13.3 in the online resources.

TEST YOURSELF: Attempt Questions 13.1–13.6 and W13.1–W13.8.

13.4 Accuracy and precision in volumetric analysis

We have already learned in Chapter 12 that instruments such as burettes, pipettes and volumetric flask are manufactured to a high degree of accuracy. This means that we can use them to measure volumes that are very close to the actual or true volume.

For example, if the correct titration figure is 25.2 cm^3 and your measurement is 25.2 cm^3, then your measurement is accurate. When measuring the concentration of ethanoic acid in vinegar using a burette, pipette and volumetric flask, provided you carry out the recommended procedure for carrying out a titration, you can be confident that the result you obtain will be accurate. In other words, the value that you calculate for the concentration of ethanoic acid in vinegar is very close to the correct or true value of ethanoic acid in vinegar.

There is another word called **precision** that we meet in our study of chemistry, which needs to be distinguished from accuracy.

For example, suppose you measure the mass of an object three times on two different laboratory balances, Figure 13.4.

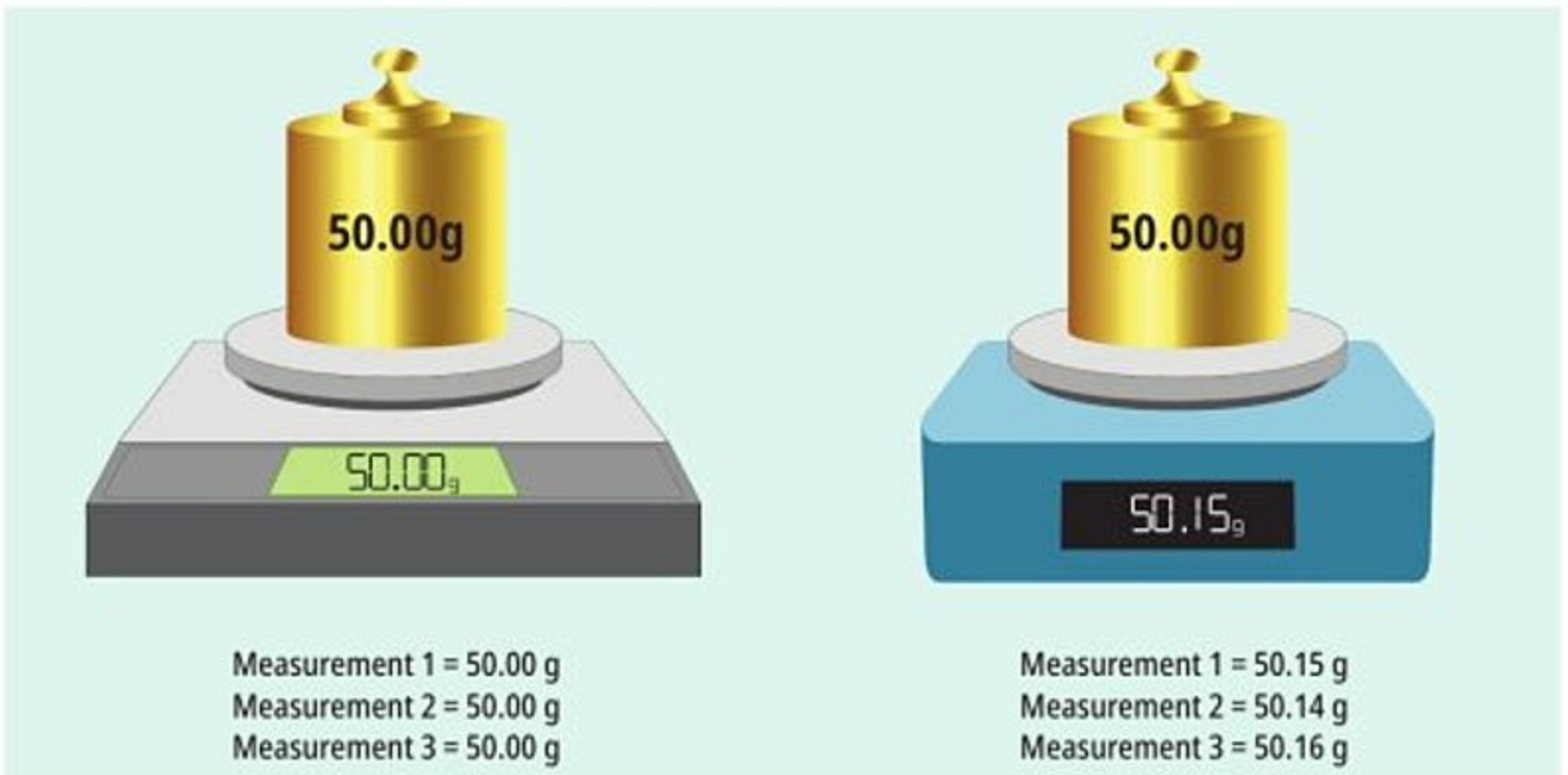


Figure 13.4 The balance on the left has been calibrated correctly at the factory and shows the true mass of 50.00 g each time a reading is taken. The balance on the right has not been calibrated correctly. It gives precise readings each time a reading is taken but they are inaccurate.

Note in Figure 13.4 that the true value of the mass is 50.00 g. The balance on the left-hand side has been properly calibrated at the factory and correctly gives the true value of 50.00 g each time a measurement is taken.

However, the balance on the right has not been calibrated properly and does not give accurate readings. Note in Figure 13.4 that all three measurements from the faulty balance are close together. We say that the measurements show **precision**. However, the fact that they do not give the true value of 50.00 g, means that there is a lack of **accuracy** in the readings of the faulty balance.

In short, accuracy means getting the correct or true result every time. Precision means getting results that are close together. **Scientists always try to obtain results that are both accurate and precise**.

Accuracy means how close a measurement is to the correct value. The correct value is often referred to as the 'true' or 'actual' value.

Precision means how close a set of repeated measurements are to each other.

Accuracy and precision are often explained using a dart board, Figure 13.5.

Some key differences between accuracy and precision are summarised in Table 13.3.

Accuracy	Precision
1. Refers to how close a measured value is to the correct value of the quantity being measured.	**1.** Refers to how close the individual measurements are with each other.
2. Focuses on the correct value.	**2.** Focuses on the repeatability of measurements.
3. Measurements are clustered around the correct value.	**3.** Measurements clustered closely together.

Table 13.3 Some differences between accuracy and precision

Why are accuracy and precision important in volumetric analysis?

When carrying out a titration, accuracy and precise measurements are of great importance because you are using the volume of one solution to determine the concentration of another solution.

- Accurate measurements of the volumes of solutions that react together will ensure that the true value of the unknown concentration of the solution being analysed will be found.
- Inaccurate measurements will lead to a wrong value of concentration.
- Precision is all about **consistency**, i.e. that you get similar results every time that you repeat the titration.
- You may recall in Chapter 12 that we mentioned that the results of two accurate titrations should agree to within 0.1 cm^3. This degree of precision tells you that your procedure is reliable, i.e. that your experimental technique is consistent. This increases the confidence in your findings.

The ability to follow a set of instructions in chemistry plays an important role in helping you to develop key laboratory skills. Following instructions exactly by using the correct masses and volumes of chemicals will help you to get accurate results. If you repeat a particular experiment, you will then get similar results, i.e. you will ensure precision in your results.

Accuracy and precision are also of importance in industrial chemistry. For example, chemists working in the pharmaceutical industry, Figure 13.6, must have the ability to follow experimental procedures very carefully. This ensures that every batch of a particular drug is made in exactly the same way so that the quality and effectiveness of the drug is maintained at the same high standards.

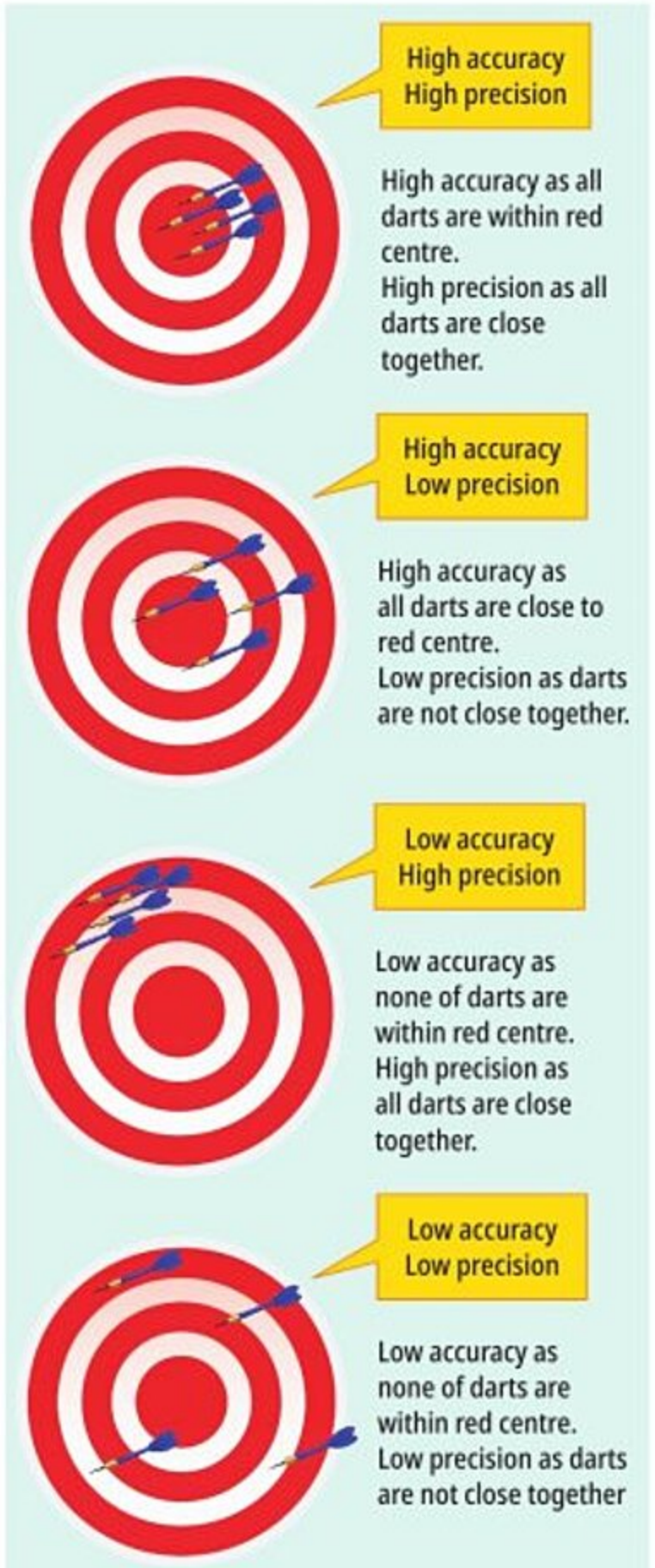

High accuracy
High precision
High accuracy as all darts are within red centre.
High precision as all darts are close together.
High accuracy
Low precision
High accuracy as all darts are close to red centre.
Low precision as darts are not close together.
Low accuracy
High precision
Low accuracy as none of darts are within red centre.
High precision as all darts are close together.
Low accuracy
Low precision
Low accuracy as none of darts are within red centre.
Low precision as darts are not close together

Figure 13.5 The game of darts can be helpful to distinguish between accuracy and precision.

Figure 13.6 Chemists working in the pharmaceutical industry must follow detailed sets of instructions as part of laboratory procedures to ensure consistency and effectiveness of drug quality from one batch to the next.

When writing up laboratory reports of practical work in volumetric analysis, it is important that you mention if your measurements are both accurate and precise. This helps others understand the reliability of your results. It also confirms that the procedure that you followed is working well.

Carrying out the wide range of experiments in the Laboratory Notebook accompanying this textbook will help you to develop key laboratory skills and achieve accurate and precise results from your work in the laboratory.

Example 13.3

Question

The correct volume of a solution is 23.0 cm^3. A student measured the volume of this solution three times and recorded the volumes as 23.5 cm^3, 23.6 cm^3 and 23.7 cm^3. Are these results accurate, precise or both?

Answer

- The results are not accurate, as they are different from the correct volume.
- The results are precise, as they are close to each other.

Example 13.4

Question

When carrying out an experiment to measure the concentration of ethanoic acid in vinegar, a student washed out the burette with deionised water but forgot to also wash it out with the solution that it was to contain. Would this error affect the accuracy, or precision, or both of the results obtained?

Answer

- This error would affect the accuracy of the results.
- The water remaining in the burette would dilute the solution of ethanoic acid placed in the burette.
- Therefore, an inaccurate titration figure would be obtained.
- The inaccurate titration figure will give an inaccurate concentration of ethanoic acid in the vinegar.
- The error will not affect the precision of the results since, while the results will be inaccurate, they will be close together.

Example 13.5

Question

A student is carrying out an experiment to measure the concentration of ethanoic acid in vinegar. What precautions should be carried out to ensure that the result obtained is as accurate as possible?

Answer

The following precautions will ensure accuracy:

1. Only use equipment which has a high degree of accuracy in measuring volumes of solutions, e.g. burette, pipette and volumetric flask.
2. Take volume readings at eye-level to prevent errors due to parallax and also read where the bottom of the meniscus touches the calibration mark.
3. Rinse glassware correctly, e.g. burettes and pipettes should first be rinsed with deionised water and then with the solutions they are to contain.
4. As you near the endpoint, add the solution drop-by-drop from the burette to obtain an accurate end point rather than overshooting the end point by adding too much solution from the burette.
5. When measuring unknown concentrations, always use standard solutions, i.e. solutions whose concentration is accurately known.

TEST YOURSELF: Attempt Questions 13.7 and W13.9–W13.18.

Summary What I should know

- Volumetric problems may be solved from first principle and also with the aid of our key formulas.
- Number of moles = $\frac{\text{Mass (in grams)}}{\text{Relative molecular Mass}}$
- Number of moles = $\frac{\text{volume* } \times \text{ molarity}}{1000}$
  (*in cm^3)
- $\frac{V_a \times M_a}{n_a} = \frac{V_b \times M_b}{n_b}$
- Density = $\frac{\text{Mass}}{\text{Volume}}$
- **Accuracy** means how close a measurement is to the correct value. The correct value is often referred to as the 'true' or 'actual' value.
- **Precision** means how close a set of repeated measurements are to each other.

Learning outcomes

At the end of this chapter, I should be able to:			
Solve acid–base volumetric problems from first principles and using key formulas.			
Explain the terms *accuracy* and *precision*.			
Discuss the reasons why accuracy and precision are important in volumetric analysis.			
Analyse data in terms of accuracy and precision.			

Chapter review questions

When answering these questions, use the values of relative atomic masses found in the *Formulae and Tables* booklet of the State Examinations Commission.

13.1 To determine the concentration of ethanoic acid in a sample of vinegar, 20.0 cm^3 of the vinegar were diluted to 200 cm^3. The diluted vinegar was titrated with a standard sodium hydroxide solution containing 1.50 g of NaOH in 500 cm^3 of solution.

On average, 22.50 cm^3 of the diluted vinegar were required to neutralise 25.0 cm^3 of this sodium hydroxide solution.

The reaction equation is:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

(a) (i) Calculate the number of moles of sodium hydroxide in each 25.0 cm^3 portion.

(ii) Calculate the number of moles of ethanoic acid per cm^3 of diluted vinegar.

(b) Find the concentration of ethanoic acid in the original vinegar **(i)** in moles per litre and **(ii)** as a percentage (w/v).

13.2 To determine the concentration of a hydrochloric acid solution, 25.0 cm^3 of this solution were diluted to 250 cm^3. The diluted acid was then titrated with a standard sodium carbonate solution containing 1.50 g of sodium carbonate, Na_2CO_3, in 500 cm^3 of solution.

On average, 20.2 cm^3 of the diluted acid were required to neutralise 25.0 cm^3 of this sodium carbonate solution.

The equation for the reaction is:

$$Na_2CO_3 + 2HCl \rightarrow 2NaCl + H_2O + CO_2$$

(a) Calculate:

(i) The number of moles of sodium carbonate in each 25.0 cm^3 portion

(ii) The number of moles of hydrochloric acid per cm^3 of diluted solution.

(b) Find the concentration of hydrochloric acid in the original solution:

(i) In terms of moles per litre

(ii) As a percentage (w/v).

13.3 A student conducted an experiment to determine the concentration of ethanoic acid in vinegar.

A 10.0 cm^3 portion of the vinegar was first diluted to exactly 50.0 cm^3. The diluted vinegar solution was titrated against a 0.08 M sodium hydroxide solution in a conical flask. 35.4 cm^3 of the diluted vinegar were required to neutralise 20.0 cm^3 of the NaOH solution.

The balanced chemical equation for the reaction is:

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

(i) Calculate the volume of undiluted vinegar required to neutralise 20.0 cm^3 of the NaOH solution.

(ii) Calculate the number of moles of sodium hydroxide in 20.0 cm^3 of solution.

(iii) Calculate the number of moles of ethanoic acid in each cm^3 of the diluted vinegar.

(iv) Calculate the concentration of ethanoic acid in the original vinegar in moles per litre.

(v) Calculate the concentration of ethanoic acid in the original vinegar in % (w/v).

13.4 A student conducted an experiment to determine the concentration of citric acid in lemon juice, Figure 13.7.

Figure 13.7 Lemon juice contains citric acid.

A 10.0 cm^3 portion of the lemon juice was first diluted to exactly 50.0 cm^3. The diluted lemon juice solution was titrated against a 0.09 M sodium hydroxide solution in a conical flask. On average, 38.5 cm^3 of the diluted lemon juice were required to neutralise 20.0 cm^3 of the NaOH solution.

The balanced equation for the reaction is:

$$C_6H_8O_7 + 3NaOH \rightarrow Na_3C_6H_5O_7 + 3H_2O$$

(a) Calculate the volume of undiluted lemon juice required to neutralise 20.0 cm^3 of the 0.09 M NaOH solution.

Chapter review questions

(b) Calculate the number of moles of sodium hydroxide in 20.0 cm^3 of solution.

(c) Calculate the number of moles of citric acid in each cm^3 of the diluted lemon juice.

(d) Calculate the concentration of citric acid in the original lemon juice in moles per litre.

(e) Calculate the concentration of citric acid in the original lemon juice in % (w/v).

13.5 A mass of 1.57 g of anhydrous sodium carbonate, Na_2CO_3, was dissolved in deionised water, and the solution was made up to 250 cm^3 in a volumetric flask. 25 cm^3 portions of this solution were titrated against 0.12 M hydrochloric acid solution. The average value for the titration figure was 29.42 cm^3

The balanced equation for the titration reaction is:

$$2HCl + Na_2CO_3 \longrightarrow 2NaCl + H_2O + CO_2$$

(a) Calculate the number of moles of HCl added to the titration flask from the burette.

(b) Hence, calculate the number of moles of Na_2CO_3 in the titration flask.

(c) Express the concentration of Na_2CO_3 in moles per litre.

13.6 To determine the concentration of a dilute solution of ammonia, Figure 13.8, a student transferred 25 cm^3 of the ammonia solution to a conical flask using a pipette.

A 0.12 M hydrochloric acid solution (density 1.04g/cm^3) was added to a burette and was titrated against the ammonia solution using 2–3 drops of a suitable indicator. After carrying out several titrations using the 25 cm^3 of ammonia solution the mean titration figure was found to be 21.33 cm^3.

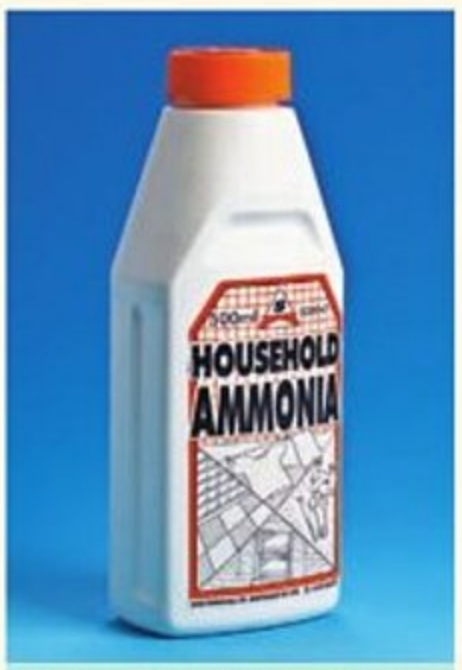


Figure 13.8 A solution of ammonia in water is commonly called ammonium hydroxide.

The balanced equation for the titration reaction is:

$$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$$

Calculate:

(a) The number of moles of hydrochloric acid in 21.33 cm^3 of the standard solution

(b) The number of moles of ammonia in the 25 cm^3 portion

(c) The concentration of ammonia in (a) moles/litre, (b) grams/litre.

13.7 **(a)** Distinguish between the terms *accuracy* and *precision*.

(b) Explain why accurate and precise measurements are important in volumetric analysis.

(c) What is meant by saying that results from a titration can be precise but not accurate?

(d) A pipette is calibrated to deliver a volume of 25.00 cm^3. However, the pipette has been damaged and consistently delivers 25.30 cm^3 of solution. Are the readings accurate, or precise, or both, or neither? Explain your answer.

(e) 'Learning to carefully follow detailed laboratory instructions and procedures is essential to achieve accurate and precise results.'

Explain the meaning of this statement and give an example of one type of chemical industry in which this statement is particularly important.

(f) 'Precision in carrying out titrations shows that your technique is consistent.'

Explain the meaning of this statement.

(g) Explain one potential consequence of not following laboratory instructions carefully when carrying out laboratory practical work in volumetric analysis.

14 Oxidation and Reduction

OBJECTIVES

- To give students an understanding of the concepts of oxidation and reduction in chemistry.
- To make students familiar with a range of oxidation and reduction reactions in our everyday lives.
- To give students an appreciation of various ways of defining oxidation and reduction in chemistry.

14.1 Introduction

One of the most famous statues in the world is the Statue of Liberty in New York Harbor. When this statue was first built in 1886, it had a shiny brown colour due to its outside layer of copper metal sheeting, Figure 14.1. However, over the years, the statue turned green as the copper reacted with oxygen and other substances in the air to form a green substance called verdigris (from the Old French meaning 'green from grey'). This type of reaction is called an oxidation reaction.

The layer of copper metal is only 2.4 mm thick. When the statue was erected it was known that the verdigris would form. In fact, the verdigris protects the copper underneath from further corrosion. If the outer sheeting were made of iron, there was a danger that it would rust away.

In the early days of chemistry, **oxidation** was defined simply as follows:

Oxidation is the addition of oxygen to a substance.

For example, when coal is burned, the chemical reaction that takes place may be described as the combining of the carbon in the coal with oxygen from the air to form the gas carbon dioxide.

carbon + oxygen → carbon dioxide

$C + O_2 \rightarrow CO_2$

carbon *gains oxygen*

∴ OXIDATION

A similar oxidation reaction occurs when magnesium metal is burned in air, Figure 14.2.

magnesium + oxygen → magnesium oxide

$2Mg + O_2 \rightarrow 2MgO$

magnesium *gains oxygen*

∴ OXIDATION

Figure 14.1 When the Statue of Liberty was gifted to the USA by France in 1886, it was a shiny brown colour due to the copper sheeting. However, over the years, the copper has reacted with oxygen and other substances in the air to form a new green substance called verdigris.

Figure 14.2 The burning of magnesium metal in air is an example of an oxidation reaction, since magnesium reacts with oxygen to form magnesium oxide.

One of the most commonly observed oxidation reactions is the rusting of iron, Figure 14.3. This may be represented in a simplified form as:

$$4Fe + 3O_2 \rightarrow 2Fe_2O_3$$

Iron *gains oxygen*

∴ OXIDATION

Corrosion is a general name used to describe the deterioration (breaking down, wearing away) of metals due to chemical reactions with their environment.

Rusting is a specific type of corrosion that occurs in iron and in its alloys such as steel. (An alloy is a mixture of one metal with another metal or with carbon. Steel is a mixture of iron and carbon.) We will be studying corrosion and its prevention in more detail in Chapter 21.

Oxygen is the most abundant element by mass in the Earth's crust and in the human body. It is also one of the most reactive elements – it combines with the vast majority of the other elements. Oxygen is involved in many of the most important chemical reactions in our lives:

- **Combustion.** The burning (combustion) of fuels is an example of an oxidation reaction, Figure 14.4. For example, methane gas burns in oxygen to form carbon dioxide and water.

$$\underset{\text{methane}}{CH_4} + \underset{\text{oxygen}}{2O_2} \rightarrow \underset{\text{carbon dioxide}}{CO_2} + \underset{\text{water}}{2H_2O}$$

Figure 14.3 Rusting is an example of an oxidation reaction. It causes the iron to form the brown oxide (Fe_2O_3) of the metal which is commonly called rust.

Corrosion is any undesired process whereby a metal is converted to one of its compounds.

Figure 14.4 The combustion of fuels is an example of an oxidation reaction. Fuels react with oxygen to form carbon dioxide and water.

- **Respiration.** You may recall when studying Junior Cycle Science that respiration is the release of energy from food in the cell of an organism. Respiration is another example of an oxidation reaction and may be described by the equation:

$$\underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{oxygen}}{6O_2} \rightarrow \underset{\text{carbon dioxide}}{6CO_2} + \underset{\text{water}}{6H_2O} + \text{Energy}$$

Therefore, it is not surprising that chemists classify many chemical reactions in terms of the reaction with oxygen.

Chemists also discovered that it was possible to remove oxygen from some substances. For example, when hydrogen gas is passed over heated copper(II) oxide, it is found that copper metal is obtained.

$$\underset{\text{copper(II) oxide}}{CuO} + \underset{\text{hydrogen}}{H_2} \rightarrow \underset{\text{copper}}{Cu} + \underset{\text{water}}{H_2O}$$

Copper(II) *loses oxygen*

∴ REDUCTION

Since this type of reaction was often used to extract metals from their ores, it was referred to as a **reduction** reaction. The reason for this name was because a large amount of an ore of the metal was converted or *reduced* to a smaller mass of metal, Figure 14.5

Note that in the above reaction the copper(II) oxide has lost oxygen. Thus, reduction could be said to be the opposite of oxidation.

Reduction may be defined as the removal of oxygen from a substance. Since hydrogen was often used to remove the oxygen, **reduction may also be defined as the addition of hydrogen**.

Figure 14.5 The word 'reduction' referred to the fact that when a metal is extracted from its ore, the mass of metal is less than the mass of the original ore.

Reduction is the removal of oxygen or the addition of hydrogen.

14.2 Oxidation and reduction in terms of electron transfer

After the discovery of the electron, chemists began to take a closer look at various chemical reactions. It became clear that many chemical reactions involved the transfer of electrons. Let us again consider the oxidation of magnesium to magnesium oxide.

$$2Mg + O_2 \rightarrow 2Mg^{2+}O^{2-}$$

Mg loses two electrons

OXIDATION

We see that what is actually happening in this reaction is that the magnesium is losing electrons and the oxygen is gaining electrons. In fact, each magnesium atom is losing two electrons. Therefore, oxidation may also be defined in terms of electron loss.

Oxidation of an element takes place when it loses electrons.

Consider now the reduction of copper(II) oxide to copper metal.

$$Cu^{2+}O^{2-} + H_2 \rightarrow Cu + H_2O$$

Cu^{2+} gains two electrons

REDUCTION

We see that what is actually happening is that the Cu^{2+} ion is gaining two electrons to become a copper atom. Thus, reduction may also be defined in terms of electron transfer.

Reduction of an element takes place when it gains electrons

The words OIL RIG ('oxidation is loss of electrons, reduction is gain of electrons') may be used to help you remember these definitions, Figure 14.6.

If we think of oxidation and reduction in terms of electrons being transferred, it becomes clear that oxidation and reduction must always occur together. If one substance loses electrons (oxidation), there must be some other substance to accept (gain) these electrons (reduction).

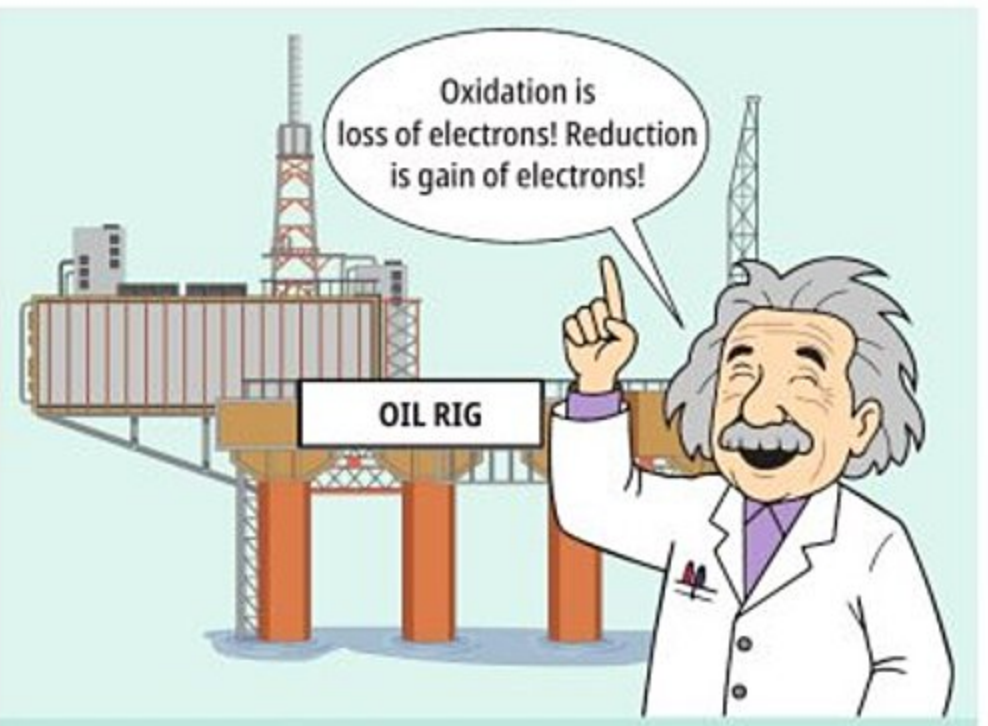
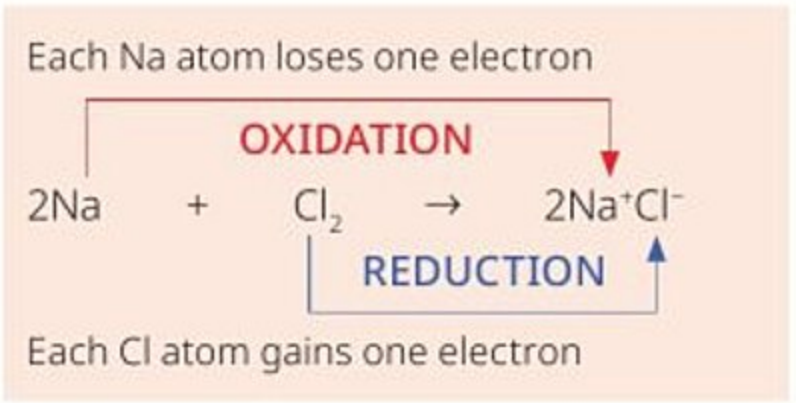


Figure 14.6 Oxidation is loss of electrons. Reduction is gain of electrons.

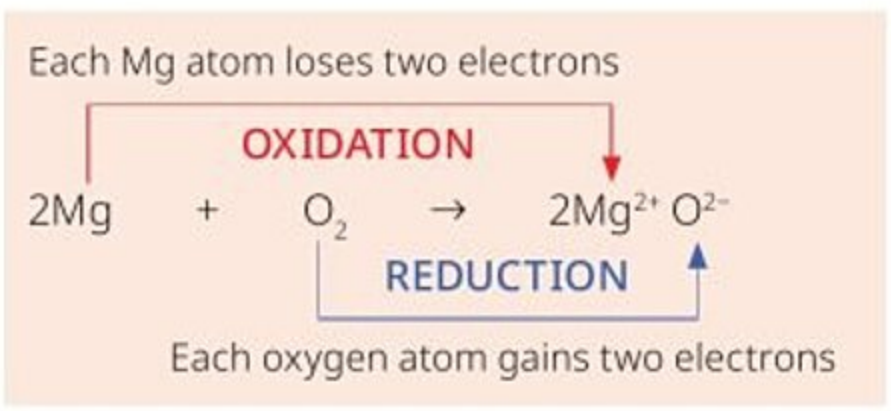
This may easily be seen in the reaction between sodium and chlorine to form sodium chloride.



A **redox reaction** is a reaction in which both oxidation and reduction take place.

- This is like a transfer of money – one person **gives** you a €10 note and you **receive** the €10 note.
- So we see that oxidation reactions and reduction reactions always occur together.
- Therefore, it is more correct to refer to these types of reactions as **oxidation–reduction** reactions or **redox** reactions.
- Note also that in the above reaction, neither oxygen nor hydrogen is present.
- It is clear, therefore, that the definitions of oxidation and reduction in terms of electron transfer are broader than the previous definitions that described oxidation and reduction in terms of oxygen and hydrogen.

If we take a closer look at the reaction between magnesium and oxygen to form magnesium oxide, we see that this is another example of an oxidation–reduction reaction.



An interesting reaction in which the results of the oxidation–reduction reaction can be easily seen is the reaction between zinc metal and copper ions, Figure 14.7.

- When zinc metal is left standing in copper sulfate solution, two observations are noted:
  - The zinc becomes covered with a brown deposit.
  - The blue colour of the solution (caused by the presence of Cu^{2+} ions) begins to fade.
- On analysing the brown deposit, it is found to be copper metal.
- This fading implies that the Cu^{2+} ions are being used up.
- On analysing the solution in the beaker, it is found that Zn^{2+} ions are present.

Chemists concluded:

- The zinc metal was being oxidised (losing electrons).
- The copper ions (Cu^{2+}) were being reduced (gaining electrons).

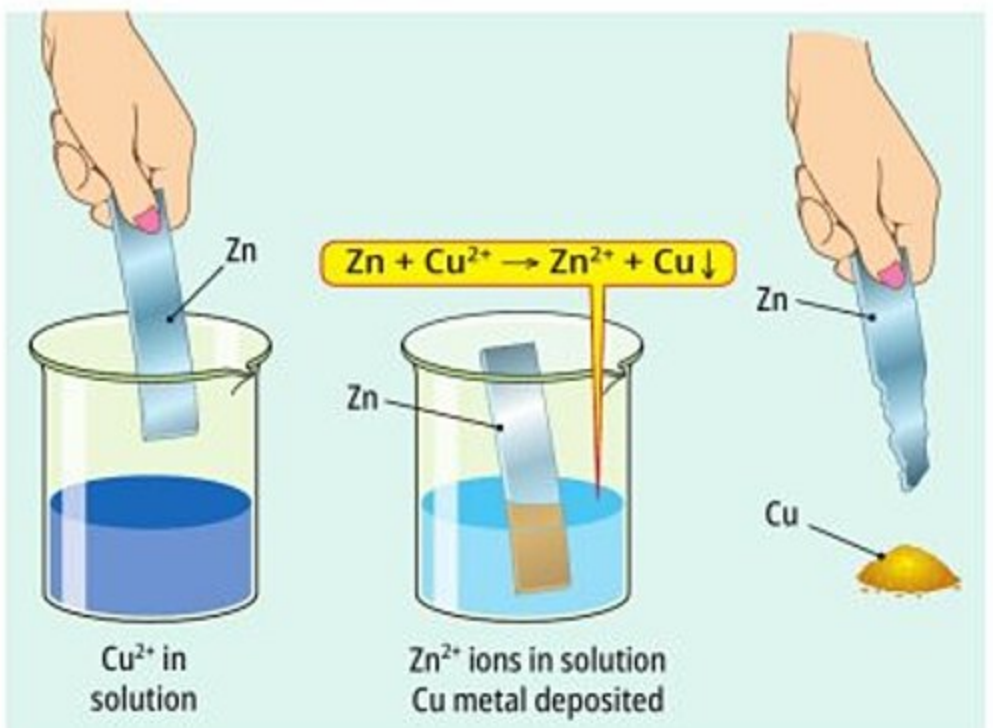


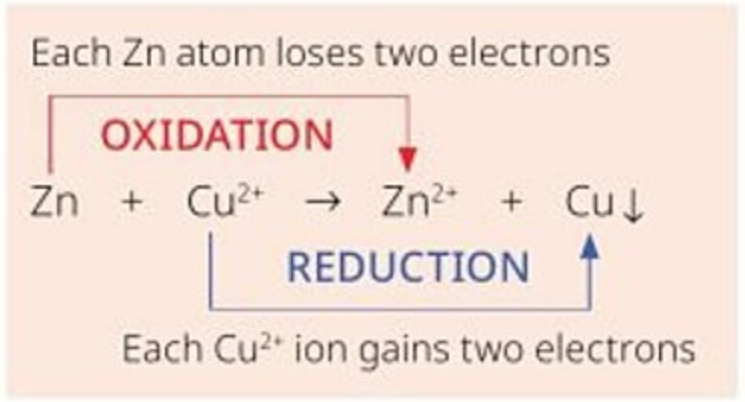
Figure 14.7 When zinc metal is left standing in a solution containing copper ions, an oxidation–reduction reaction takes place. This reaction causes copper metal to be deposited, and zinc goes into solution as Zn^{2+} ions.

The above evidence led chemists to conclude that the following chemical reaction was taking place:

$$Zn + Cu^{2+} \rightarrow Zn^{2+} + Cu \downarrow$$

Recall that the downward arrow after Cu means that the copper settles out of solution. An insoluble solid that settles out of solution is called a **precipitate**.

If we study this equation closely, we see that the Zn is oxidised and the Cu^{2+} is reduced:



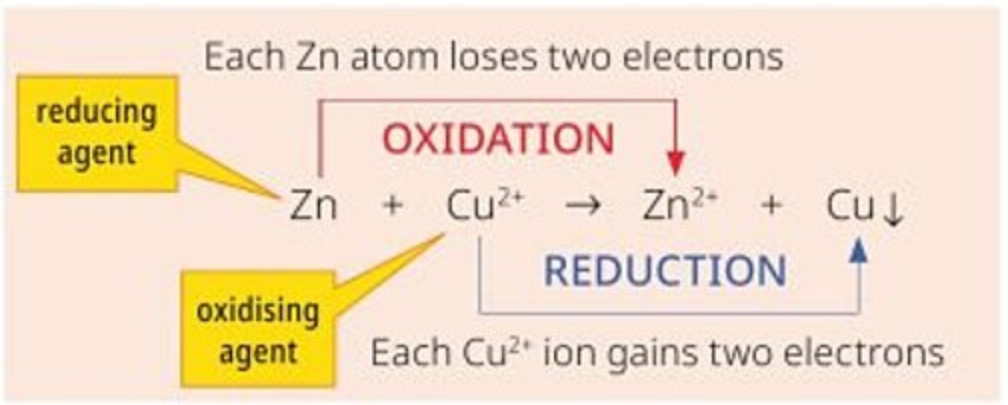
In this reaction, the zinc atom could not lose electrons (oxidation) without the presence of something to accept (gain) these electrons (i.e. the Cu^{2+} ion). We say that the Cu^{2+} ion is **an oxidising agent**. (Another name for an oxidising agent is **oxidant**.) An agent is someone or something that undertakes a mission to get things done. In redox reactions, the oxidising agents have a mission to bring about oxidation, i.e. to take electrons from another species.

An **oxidising agent** is a substance that brings about oxidation in other substances.

- If we look at the above equation, we see that the Cu^{2+} ion (the oxidising agent) accepts two electrons from the Zn atom i.e. the Cu^{2+} ion is itself reduced.
- This is a general characteristic of oxidising agents – **the oxidising agent is always reduced**.
- The substance that causes the Cu^{2+} ion to be reduced is Zn.
- Therefore, we say that Zn is the **reducing agent**. (Another name for a reducing agent is a **reductant**.) In redox reactions, the reducing agents have a mission to bring about reduction, i.e. to add electrons to another species.
- In order for a substance to act as a reducing agent, it must donate electrons to some other substance, e.g. in the above equation Zn gives two electrons to the Cu^{2+} ion.
- When it does this, the Zn itself is oxidised.
- This is a general characteristic of reducing agents – **the reducing agent is always oxidised**.

A **reducing agent** is a substance that brings about reduction in other substances.

We can now indicate the oxidising and reducing agents in the above equation.



A common oxidising agent is hydrogen peroxide, H_2O_2, which is used to bleach hair. The hydrogen peroxide converts the coloured pigment in the hair to a colourless hair 'pigment' that leaves the hair blonde – hence the expression 'peroxide blonde', Figure 14.8. The hydrogen peroxide solution used in hair salons is usually only about 3% w/v concentration. This is much more dilute than the concentrated solution of hydrogen peroxide that you find in laboratories.

Figure 14.8 Hydrogen peroxide is a very useful oxidising agent. It oxidises the coloured pigments in hair to a blonde colour.

Some everyday examples of oxidising agents are summarised in Table 14.1.

Oxidising agent	Use	Reaction
Hydrogen peroxide, H_2O_2	Bleaching hair	coloured hair pigment + H_2O_2 → colourless hair 'pigment' + H_2O
Iodine, I_2	Used to prevent infection of cuts; a solution of iodine in ethanol is called 'tincture of iodine'	live germ + I_2 → $2I^-$ + dead germ
Chlorine gas, Cl_2	Used in treating water to make it safe to drink	live germ + Cl_2 → $2Cl^-$ + dead germ
Sodium hypochlorite, NaClO	Household bleach for bleaching clothes	coloured fabric + ClO^- → Cl^- + colourless fabric

Table 14.1 Examples of oxidising agents.

Some examples of reducing agents are summarised in Table 14.2.

Reducing agent	Use	Reaction
Carbon	Used to extract metals from their ores by removing oxygen from the ore	Fe_2O_3 + 3C → 2Fe + 3CO iron ore → iron metal
Aluminium	Used to extract metals from their ores by removing oxygen from the ore	Fe_2O_3 + 2Al → 2Fe + Al_2O_3 iron ore → iron metal
Sulfur dioxide, SO_2	Used as a food preservative (E220) as it prevents the oxidation of natural sugars (food spoilage); also used in bleaching items, e.g. paper and textiles	Coloured form of dye + sulfur dioxide → colourless form of dye
Vitamin C (Ascorbic acid)	Vitamin C acts as a reducing agent by converting insoluble Fe^{3+} ions into soluble Fe^{2+} ions; this helps iron to be absorbed in the body	Fe^{3+} + vitamin C → Fe^{2+}

Table 14.2 Examples of reducing agents

Example 14.1

Question

Define oxidation in terms of electron transfer. In the following example, indicate clearly, by showing electron loss or gain, which species is being oxidised and which is being reduced:

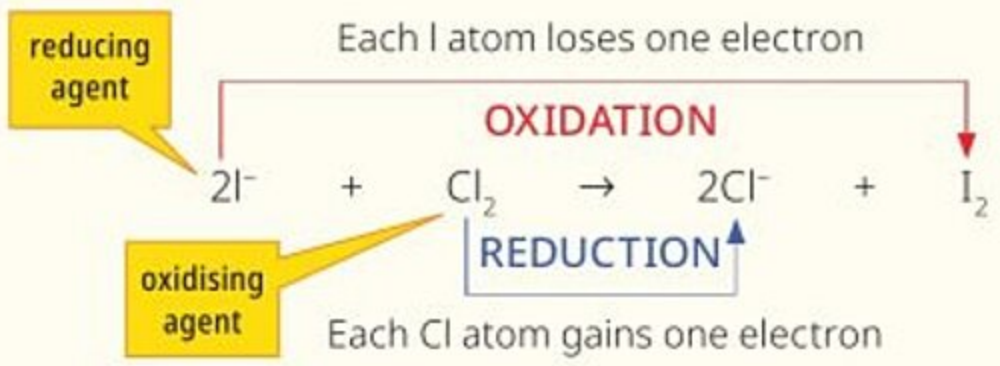
$2KI + Cl_2 \rightarrow 2KCl + I_2$

What are the oxidising and reducing agents in the above reaction? [LCH]

Answer

Oxidation is the loss of electrons.

The electron loss and electron gain may be more easily seen if we ignore the K^+ ion ('spectator ion') on each side of the equation. All of the required information may then be summarised as follows:



- Once you have established what is oxidised and what is reduced, it is easy to pick out the oxidising and reducing agents.
- In this question, since the I^- is oxidised, the oxidising agent must be the Cl_2.
- Similarly, since the Cl_2 is reduced, the reducing agent must be I^-.
- The question merely asks you to indicate the various items, so full marks are obtained for laying out your work as shown above.

14.3 Oxidation numbers: Keeping track of electrons

TEST YOURSELF: Attempt Questions 14.1 and 14.2.

As chemistry developed, it became clear that the definitions of oxidation and reduction needed to be expanded further. We have already seen that oxidation–reduction reactions need not involve oxygen at all. It was also found that not all oxidation–reduction reactions involved electron transfer, i.e. ionic compounds were not formed in all redox reactions.

Consider, for example, the reaction between hydrogen and oxygen:

$$2H_2 + O_2 \rightarrow 2H_2O$$

This reaction is very different from the reaction of magnesium with oxygen as no ions are formed. Water is a covalent compound.

- To keep track of the movement of electrons during chemical reactions in which covalent compounds are involved, chemists introduced the idea of **oxidation numbers** (also called **oxidation states**).
- Oxidation numbers are simply numbers that are assigned to atoms to help us decide whether or not oxidation and reduction have taken place and, if so, how many electrons have been lost and gained.

Oxidation number is the charge that an atom has or appears to have when electrons are distributed according to certain rules.

Oxidation number is also described as the charge that an atom appears to have in a compound if the bonding is assumed to be completely ionic.

For example, in the compound water, the two electrons in each of the single covalent bonds are counted as if they have been completely transferred to the more electronegative element, i.e. to the oxygen atom (E.N. of H = 2.20, E.N. of O = 3.44), Figure 14.9.

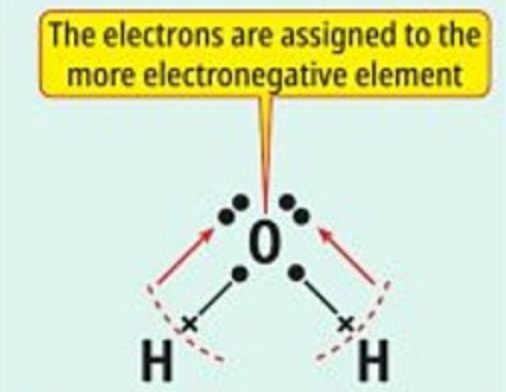


Figure 14.9 When assigning oxidation numbers, the electrons are assigned to the more electronegative element.

Since we have 'transferred ownership' (on paper) of two electrons from hydrogen to oxygen, we assign an oxidation number of –2 to the oxygen atom. Since each hydrogen atom has formally lost an electron, we assign an oxidation number of +1 to each of the hydrogen atoms. This may be indicated by writing:

$$\underset{2(+1)\ -2}{H_2O}$$

Since oxidation numbers are not actual charges, they are usually written under the symbol of the element. This avoids confusion when dealing with charged species.

Chemists have developed rules to make it easy for us to assign oxidation numbers. We will now discuss these rules.

Rules for assigning oxidation numbers

1. **The oxidation number of any uncombined element is zero.**
   - An uncombined element is an element that is not bonded to another element, e.g. Zn, Fe, O_2 and Cl_2.
   - This means that in H_2 the oxidation number (O.N.) of hydrogen is zero, in sodium metal (Na) the O.N. of Na is 0 and in F_2 the O.N. of F is 0.
2. **The oxidation number of an ion of an element is the same as its charge.**
   - This means that the O.N. of Br in the Br^- ion is –1
   - The O.N. of Fe in Fe^{2+} is +2
   - The O.N. of Na in Na^+Cl^- is +1
   - The O.N. of Cl in Na^+Cl^- is –1
   - The O.N. of Mg in $Mg^{2+}O^{2-}$ is +2
3. **The sum of the oxidation numbers of all the elements in a compound must add up to zero.**
   - For example, in NaCl the sum of the oxidation numbers is +1 (for sodium) added to –1 (for chlorine) to give a total of zero.
   - Similarly, in H_2O the sum is 2(+1) for the hydrogen atoms added to –2 for the oxygen atom, giving a total of zero.

4. **Oxygen always has an oxidation number of –2. There are two exceptions. In peroxides it has an oxidation number of –1 and in the compound OF_2 it has an oxidation number of +2.**

- In magnesium oxide, $Mg^{2+}O^{2-}$, the oxidation number of oxygen is –2.
- **First exception to rule:** In hydrogen peroxide, H_2O_2, the oxygen is assigned an oxidation number of –1. This is done in order that the sum of all of the oxidation numbers in H_2O_2 will add up to zero, i.e. 2(+1) for the two hydrogen atoms and 2(–1) for the two oxygen atoms.
- **Second exception to rule:** A similar reason holds in the case of oxygen difluoride, OF_2. Fluorine is the only element that is more electronegative than oxygen. Therefore, in the OF_2 molecule, Figure 14.10, the electrons in the two covalent bonds are assigned to the fluorine atoms. Therefore, so that the sum of all of the oxidation numbers adds up to zero, the oxygen atom must be assigned an oxidation number of +2.

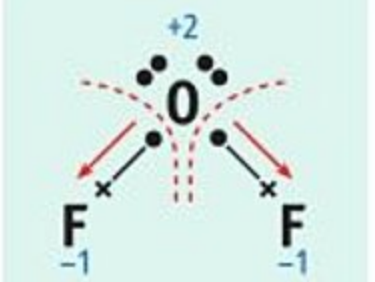


Figure 14.10 Oxygen has an oxidation number of +2 in oxygen difluoride.

5. **Hydrogen is always assigned an oxidation number of +1 in its compounds. There is one exception. In the metal hydrides it is assigned the metal hydrides it is assigned an oxidation number of –1.**

- For example, in NH_3 each H atom is assigned an oxidation number of +1. It follows from Rule 3 above that the oxidation number of the N atom must be –3.
- **Exception to rule:** In a metal hydride (e.g. NaH) the H atom is assigned an oxidation number of –1. The reason for this is because sodium hydride is an ionic compound, Na^+H^-. The oxidation number of –1 is assigned to the H atom because there is one negative charge on this atom (Rule 2).

6. **The halogens always have an oxidation number of –1 in their compounds unless bonded to a more electronegative atom.**

- For example, since fluorine is the most electronegative element in the Periodic Table, its oxidation number will always be –1.
- Although chlorine usually has an oxidation number of –1 in its compounds, this is not the case when it is bonded to oxygen or fluorine both of which are more electronegative than chlorine. (E.N. of O = 3.44, E.N. of F = 3.98, E.N. of Cl = 3.16).
- For example, in Cl_2O the oxidation number of each chlorine atom is +1. In the compound Cl_2O_7, each chlorine atom has an oxidation number of +7.

Cl_2O	Cl_2O_7
2(+1) –2	2(+7) 7(–2)
O.N. of Cl = +1	O.N. of Cl = +7

- Thus, whereas the O.N. of fluorine is always –1, the O.N. of the other halogens can vary depending on the particular compound.
- Note the difference in the way that the formulas OF_2 and Cl_2O are written. As a general rule, the more electronegative element is usually placed second.

7. **In a compound that is composed of two different elements, the electrons are assigned to the more electronegative element. The oxidation number of the second element is calculated by balancing the overall charge on the molecule.**

   - For example, consider the compound CS_2, Figure 14.11. This compound has the same structure as CO_2.
   - Since the E.N. value of sulfur (2.58) is greater than the E.N. value of carbon (2.55), the four outer electrons of carbon are formally assigned to sulfur.
   - Therefore the oxidation number of each sulfur atom = –2.
   - This gives a total negative charge of –4.
   - Therefore, the O.N. of C = +4 to balance the charges so that the overall sum of oxidation numbers add up to 0.

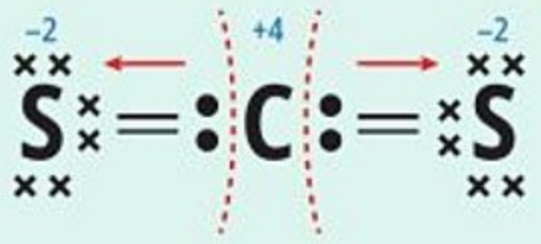


Figure 14.11 In carbon disulfide, since the E.N. value of sulfur is great than that of carbon, the four outer electrons of carbon are formally assigned to sulfur.

8. **The sum of the oxidation numbers of all the elements in a polyatomic ion must equal the charge on the ion.**

   - A polyatomic ion consists of two or more atoms bonded together and functions as a single unit with an overall charge. We have already met polyatomic ions in Experiment 5.1, e.g. NO_3^-, SO_4^{2-} and CO_3^{2-}. (Ions such as Cl^-, Na^+ and Mg^{2+} are often referred to as **simple ions**.)
   - The following example will illustrate the usefulness of this rule.

Note: Some elements nearly always have the same oxidation number in their compounds. Such elements are the alkali metals (Li, Na, K, etc.) which have an oxidation number of +1. Similarly, the alkaline earth metals (Be, Mg, Ca, etc.) have an oxidation number of +2. You will find that the oxidation numbers of these two groups of elements will be very useful as reference points for assigning oxidation numbers to elements in their compounds.

Example 14.2

Question

What is the oxidation number of the N atom in the NO_3^- ion?

Answer

- We know that the oxidation number of the O atom is –2.
- Therefore, the negative charge due to three oxygen atoms is $3 \times (-2) = -6$
- But overall charge on ion = –1
- From rule 8, adding the oxidation number of the N atom to –6 must equal –1.
- Let x = oxidation number of the N atom.
  $x + (-6) = -1$
  $x = -1 + 6 = 5$

$$\underset{+5}{N}O_3^{\underset{3(-2)}{-}}$$

O.N. of the N atom = 5

Example 14.3

Question

What is the oxidation number of each of the elements in $CuSO_4$?

Answer

- Note that of the three elements in $CuSO_4$, only one (oxygen) is mentioned in the rules for assigning oxidation numbers.
- To work out the oxidation numbers of Cu and S, we need to know that there are two negative charges on the sulfate ion, i.e. SO_4^{2-}.
- This must mean that, in order to balance the charges, there must be two positive charges on the copper, i.e. Cu^{2+}.
- Therefore, the oxidation number of copper is +2.
- Now consider the SO_4^{2-} ion. The four oxygen atoms give a total negative charge of 4(–2) = –8.
- The overall charge on the ion is –2.
- Therefore, the oxidation number of the sulfur atom must be +6.

$$\underset{+2}{Cu}\underset{+6}{S}\underset{4(-2)}{O_4}$$

EXAM TIP!

It is always best to clearly state the oxidation numbers of the elements. In the above notation, it is not clear if the oxidation number of oxygen is 4 or –2. To avoid any confusion in an exam, it is best to set out your work as follows:

$$\underset{+2}{Cu}\underset{+6}{S}\underset{4(-2)}{O_4}$$

O.N. of Cu = +2 O.N. of S = +6 O.N. of O = –2

In Example 14.3, copper has an oxidation number of +2. Since transition metals exhibit variable valency, the oxidation number of copper varies, e.g. in Cu_2O the oxidation number of Cu is +1, Figure 14.12.

We have already discussed the naming of transition metal compounds in Chapter 5. A summary of some examples is given in Table 14.3. The oxidation number (written in Roman numerals) is used in naming these compounds, e.g. FeO is called iron(II) oxide and Fe_2O_3 is called iron(III) oxide. Another way of stating this is to say that iron exists in an oxidation state of two (+2) and an oxidation state of three (+3). In short, the Roman numeral tells us the oxidation state of the element.

Figure 14.12 Copper(I) oxide is so called because copper has an oxidation number of 1 in Cu_2O. Copper has an oxidation number of 2 in copper(II) oxide, CuO.

Formula of compound	Oxidation number of transition metal	Name of compound
Cu_2O	Cu = +1	Copper(I) oxide
CuO	Cu = + 2	Copper(II) oxide
FeO	Fe = +2	Iron(II) oxide
Fe_2O_3	Fe = + 3	Iron (III) oxide
MnO_2	Mn = +4	Manganese(IV) oxide – commonly called *manganese dioxide*
$KMnO_4$	Mn = +7	Potassium manganate(VII) – commonly called *potassium permanganate*
V_2O_3	V = +3	Vanadium(III) oxide
V_2O_5	V = +5	Vanadium(V) oxide
Cr_2O_3	Cr = +3	Chromium(III) oxide
$K_2Cr_2O_7$	Cr = + 6	Potassium dichromate(VI)

Table 14.3 Examples of transition metal compounds

Although we have only shown two oxidation states for each metal in Table 14.3, some elements have more than two oxidation states. For example, the metal vanadium has four oxidation states, Figure 14.13.

In your Leaving Certificate exam, you will only be asked to assign oxidation numbers up to the first 36 elements.

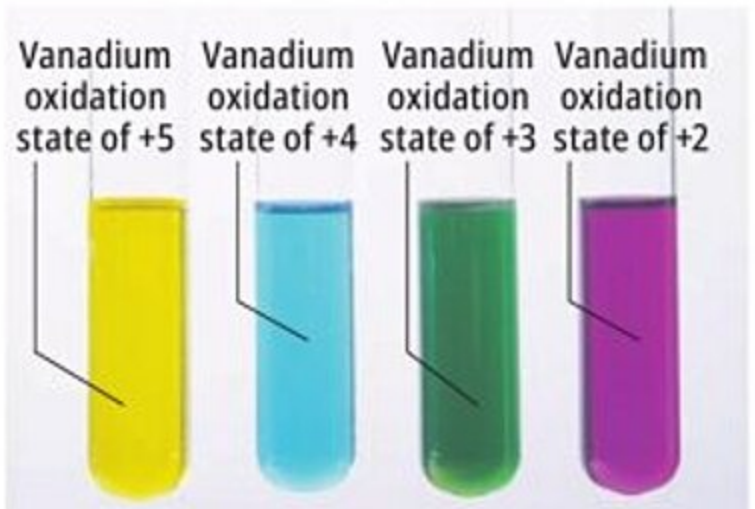

Vanadium oxidation state of +5
Vanadium oxidation state of +4
Vanadium oxidation state of +3
Vanadium oxidation state of +2

Figure 14.13 Vanadium exists in four oxidation states.

Example 14.4

Question

What is the oxidation number of sulfur in $Na_2S_2O_3$?

Answer

Each sodium atom has an oxidation number of +1.

Each oxygen atom has an oxidation number of –2.

$$\mathbf{Na_2S_2O_3}$$

$$2(+1)\ 2(x)\ 3(-2)$$

Let x = oxidation number of sulfur. The sum of all the oxidation numbers must be zero.

$2(+1) + 2x + 3(-2) = 0$

$2x = 6 - 2 = 4$

$x = 2$

Oxidation number of sulfur = +2

Since oxidation numbers are assigned to help us 'keep track' of electrons on paper, we sometimes find that when we apply the rules, the oxidation number of an element may not work out to be a whole number. This is the case in Example 14.5.

Example 14.5

Question

What is the oxidation number of sulfur in $Na_2S_4O_6$?

Answer

Each sodium atom has an oxidation number of +1.

Each oxygen atom has an oxidation number of –2.

$$\underset{2(+1)}{Na_2}\ \underset{4(x)}{S_4}\ \underset{6(-2)}{O_6}$$

Let x = oxidation number of sulfur. The sum of all the oxidation numbers must be zero.

$2(+1) + 4x + 6(-2) = 0$

$4x = 12 - 2 = 10$

$x = 2.5$

Oxidation number of sulfur = +2.5

Note:

1. You may wonder what an oxidation number of 2.5 means. The 2.5 can be thought of as an average value of the oxidation numbers of the sulfur atoms. Not all atoms of sulfur in the $Na_2S_4O_6$ molecule are bonded in an identical way. This means that some S atoms have a different oxidation number than other S atoms. The average oxidation number works out as 2.5.
2. There are cases where an element may have an oxidation number of 0 even when it is in a compound, e.g. C has an oxidation number of 0 in sucrose, $C_{12}H_{22}O_{11}$.
3. Note the distinction between valency and oxidation number. You may remember that we explained valency in Chapter 5 in terms of the number of atoms of hydrogen or any other monovalent element with which each atom of the element combines. Valency is just a number and does not carry any plus or minus charge. For example, the valency of carbon is 4 because it combines with four hydrogen atoms as in CH_4. However, oxidation numbers can be positive or negative or zero. For example, the oxidation number of carbon in CH_4 is –4, in CCl_4 it is +4, and in CH_2Cl_2 it is 0.

Another difference between valency and oxidation number is that valency is always a whole number but oxidation numbers can be fractions.

TEST YOURSELF: Attempt Questions 14.3–14.5 and W14.1–W14.8.

When an element is oxidised, its oxidation number increases, i.e. **oxidation is an increase in oxidation number.**

When an element is reduced, its oxidation number decreases, i.e. **reduction is a decrease in oxidation number.**

14.4 Oxidation and reduction in terms of oxidation numbers

Oxidation numbers may be used to give very comprehensive definitions of oxidation and reduction.

The use of oxidation numbers to determine the species that are oxidised and reduced is shown in Examples 14.6 and 14.7.

Example 14.6

Question

Using oxidation numbers, indicate the species oxidised and reduced in the reaction:

$2H_2 + O_2 \rightarrow 2H_2O$

Answer

Assign oxidation numbers and indicate the elements that change oxidation number.

Increase in oxidation number

OXIDATION

$$\underset{0}{2H_2} + \underset{0}{O_2} \rightarrow \underset{+1\ -2}{2H_2O}$$

REDUCTION

Decrease in oxidation number

Example 14.7

Question

Use oxidation numbers to determine whether or not the following is an oxidation/reduction reaction and, if so, indicate which species is being oxidised and which is being reduced:

$Cu + 2H_2SO_4 \rightarrow CuSO_4 + SO_2 + 2H_2O$ [LCH]

Answer

Step 1

Write under each element the oxidation number of that element (using a pencil).

$$\underset{0}{Cu} + \underset{2(+1)\ +6\ 4(-2)}{2H_2SO_4} \rightarrow \underset{+2\ +6\ 4(-2)}{CuSO_4} + \underset{+4\ 2(-2)}{SO_2} + \underset{2(+1)-2}{2H_2O}$$

Step 2

Mark (in ink) those elements that show a change in oxidation number.

$$\underset{0}{Cu} + 2H_2\underset{+6}{S}O_4 \rightarrow Cu\underset{+2}{S}O_4 + \underset{+4}{S}O_2 + 2H_2O$$

It now becomes clearer which elements are oxidised and which are reduced. Note that in particular example, one of the sulfur atoms is neither oxidised nor reduced (O.N. of S = +6 in both H_2SO_4 and $CuSO_4$) and the other sulfur atom is reduced (O.N. of S in H_2SO_4 = +6, O.N. of S in SO_2 = +4).

Increase in oxidation number

OXIDATION

$$\underset{0}{Cu} + \underset{+6}{2H_2S}O_4 \rightarrow Cu\underset{+2}{S}O_4 + \underset{+4}{S}O_2 + 2H_2O$$

REDUCTION

Decrease in oxidation number

In this example, sulfuric acid is the oxidising agent (and is therefore reduced) and copper is the reducing agent (and is therefore oxidised).

TEST YOURSELF: Attempt Questions 14.6 – 14.7 and W14.9–W14.13.

14.5 Balancing redox equations

In Section 10.4 we learned how to balance equations by inspection. This trial-and-error approach is fine for fairly simple equations. However, for more complicated equations, it is preferable to balance the equations in a more systematic manner. In the case of oxidation–reduction reactions, we use oxidation numbers to help us balance the equation.

The method is illustrated in the following examples.

Example 14.8

Question

Using oxidation numbers, balance the following equation:

$MnO_4^- + Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

Answer

Step 1

Assign oxidation numbers to all atoms.

$$\underset{+7}{MnO_4^-} + \underset{+2}{Fe^{2+}} + \underset{+1}{H^+} \rightarrow \underset{+2}{Mn^{2+}} + \underset{+3}{Fe^{3+}} + \underset{2(+1)\,-2}{H_2O}$$

$4(-2)$

Step 2

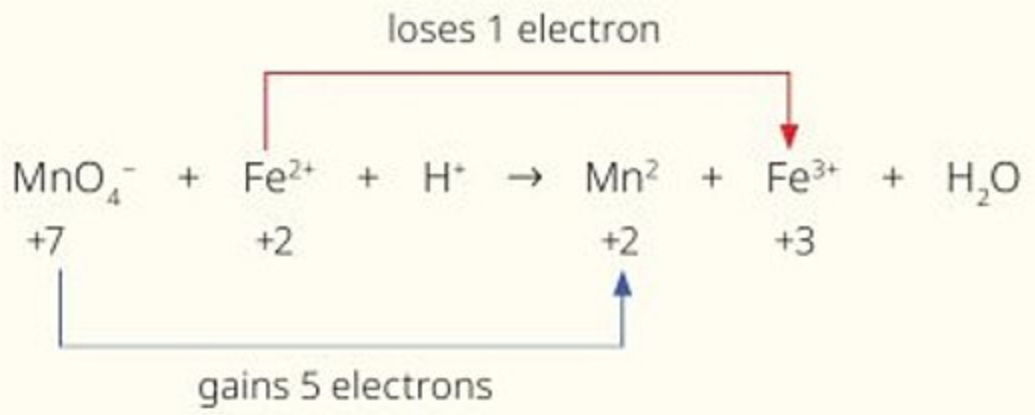
Note which elements change oxidation number.

$$\underset{+7}{MnO_4^-} + \underset{+2}{Fe^{2+}} + H^+ \rightarrow \underset{+2}{Mn^{2+}} + \underset{+3}{Fe^{3+}} + H_2O$$

Step 3

Show the number of electrons lost and gained.

An increase in oxidation number represents a loss of electrons. A decrease in oxidation number represents a gain of electrons.



Step 4

Work out the ratio of oxidising agent to reducing agent.

In Step 3, we see that each MnO_4^- ion must gain five electrons from the Fe^{2+} ion. However, each Fe^{2+} ion can only lose one electron. Therefore, there must be five Fe^{2+} ions for every one MnO_4^- ion, i.e. MnO_4^- and Fe^{2+} react in the ratio of 1 : 5.

Therefore, we can write:

$1MnO_4^- + 5Fe^{2+} + H^+ \rightarrow Mn^{2+} + Fe^{3+} + H_2O$

(The '1' before the MnO_4^- is usually omitted. It is written in here just to emphasise the ratio.)

Step 4 is a vital step. Therefore, it is best to just concentrate on getting this ratio correct and forget about everything else in the equation.

Step 5

Balance the remaining items in the equation by the inspection method.

As a general rule, leave oxygen and hydrogen atoms as the last items to be balanced. From the above, we see that there is one Mn atom on the left-hand side (L.H.S) of the equation. Therefore, there must be one Mn atom on the right-hand side (R.H.S) of the equation.

$1MnO_4^- + 5Fe^{2+} + H^+ \rightarrow 1Mn^{2+} + Fe^{3+} + H_2O$

Similarly, there are five iron atoms on the L.H.S. Therefore, there must be five iron atoms on the R.H.S.

$1MnO_4^- + 5Fe^{2+} + H^+ \rightarrow 1Mn^{2+} + 5Fe^{3+} + H_2O$

There are four oxygen atoms on the L.H.S. Therefore, there must be four oxygen atoms on the R.H.S.

$1MnO_4^- + 5Fe^{2+} + H^+ \rightarrow 1Mn^{2+} + 5Fe^{3+} + 4H_2O$

Finally, there are eight hydrogen atoms on the R.H.S. Therefore, there must be eight H atoms on the L.H.S.

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Always double check that the equation is balanced for atoms. If the equation involves ions, also check that the equation is balanced for charges

1. **For atoms:**

	L.H.S.	R.H.S.
Mn	1	1 ✓
Fe	5	5 ✓
O	4	4 ✓
H	8	8 ✓

2. **For charges:**

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$	
Charge on L.H.S = 1(–1) + 5(+2) +8(+1) = +17	Charge on R.H.S. = 1(+2) +5(+3) +4(0) = +17

EXAM TIP!

It is important that you use oxidation numbers to balance oxidation–reduction equations.

You would be very unlikely to obtain the correct ratio of oxidising agent to reducing agent if you simply attempted to balance the equation by inspection.

Also, ensure that you indicate the correct charges on each of the species in the equation, as even one incorrect charge can lose many marks!

Example 14.9

Question

Using oxidation numbers, balance the following equation:

$Cu + HNO_3 + H^+ \rightarrow Cu^{2+} + NO + H_2O$

Answer

Step 1

Assign oxidation numbers to all atoms.

Cu	+	HNO_3	+	H^+	→	Cu^{2+}	+	NO	+	H_2O
0		+1+5 3(–2)		+1		+2		+2–2		2(+1) –2

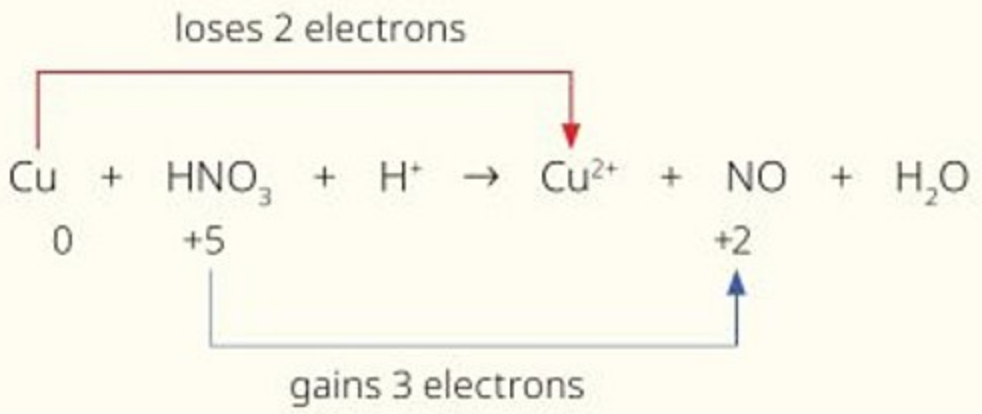
Step 2

Note which elements change oxidation number.

Cu	+	HNO_3	+	H^+	→	Cu^{2+}	+	NO	+	H_2O
0		+5				+2		+2		

Step 3

Show the number of electrons lost and gained.



Step 4

Work out the ratio of oxidising agent to reducing agent.

In order to have the same number of electrons lost and gained, bring this number up to six, i.e. 3Cu and $2HNO_3$.

$3Cu + 2HNO_3 + H^+ \rightarrow Cu^{2+} + NO + H_2O$

Step 5

Balance the remaining items in the equation by the inspection method.

$3Cu + 2HNO_3 + 6H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$

Double check that the equation is balanced using tables for atoms and charges.

1. For atoms:

	L.H.S.	R.H.S.
Cu	3	3 ✓
N	2	2 ✓
O	6	6 ✓
H	8	8 ✓

2. For charges:

$3Cu + 2HNO_3 + 6H^+ \rightarrow 3Cu^{2+} + 2NO + 4H_2O$	
Charge on L.H.S. = 6(+1) = +6	Charge on R.H.S = 3(+2) = +6

» Study Example 14.10 in the online resources.

Example 14.11

Question

Using oxidation numbers, balance the following equation:

$I_2 + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$

Answer

Step 1

Assign oxidation numbers to all atoms.

I_2	+	$S_2O_3^{2-}$	→	I^-	+	$S_4O_6^{2-}$
0		2(+2) 3(−2)		−1		4(+2.5) 6(−2)

Step 2

Note which elements change oxidation number.

I_2	+	$S_2O_3^{2-}$	→	I^-	+	$S_4O_6^{2-}$
0		+2		−1		+2.5

Step 3

Show the number of electrons lost and gained.

Each S atom loses '0.5' electrons

∴ the $S_2O_3^{2-}$ ion loses 1 electron

I_2	+	$S_2O_3^{2-}$	→	I^-	+	$S_4O_6^{2-}$
0		+2		−1		+2.5

Each I atom gains 1 electron

∴ I_2 gains 2 electrons

Step 4

Work out the ratio of oxidising agent to reducing agent.

In order to have the same number of electrons lost and gained, we need two $S_2O_3^{2-}$ ions for every one molecule of I_2.

$$I_2 + 2S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$$

Step 5

Balance the remaining items in the equation by the inspection method.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

TEST YOURSELF: Attempt Questions 14.8–14.9 and W14.14–W14.25.

Double check that the equation is balanced using tables for atoms and charges.

1. For atoms:

	L.H.S.	R.H.S.
I	2	2 ✓
S	4	4 ✓
O	6	6 ✓

2. For charges:

$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$	
Charge on L.H.S. = 2(−2) = −4	Charge on R.H.S = 2(−1) + 1(−2) = −4

» Study SEC exam question 14.12 and model answer in the online resources.

Summary What I should know

- Oxidation is the addition of oxygen to a substance.
- Reduction is the removal of oxygen from a substance or the addition of hydrogen to a substance.
- Oxidation of an element takes place when it loses electrons.
- Reduction of an element takes place when it gains electrons.
- An oxidising agent is a substance that brings about oxidation in other substances.
- A reducing agent is a substance that brings about reduction in other substances.
- Oxidation number is the charge that an atom has or appears to have when electrons are distributed according to certain rules.
- Oxidation is an increase in oxidation number.
- Reduction is a decrease in oxidation number.
- Oxidation numbers may be used to balance redox equations.

Learning outcomes

At the end of this chapter, I should be able to:

Explain oxidation in terms of the addition of oxygen to a substance, the loss of electrons and an increase in oxidation number.	
Explain reduction in terms of removal of oxygen from a substance, the addition of hydrogen, the gain of electrons and a decrease in oxidation number.	
Discuss the terms *oxidising agent* and *reducing agent*.	
Apply the rules for assigning oxidation numbers and balance redox equations.	

Chapter review questions

14.1

(a) Why did the copper in the Statue of Liberty turn green over many years?

(b) Define oxidation in terms of electron transfer. [LCH]

(c) What is an oxidising agent?

(d) What oxidising agent do household bleaches usually contain?

(e) What would you observe when a piece of zinc is left for some hours in an aqueous solution of copper(II) sulfate? [LCH]

(f) Chlorine is an example of what type of agent?

(g) Name the oxidising agent that is commonly used to bleach hair.

(h) Tincture of iodine is a solution of iodine in what substance?

(i) What is usually added in small amounts to drinking water to kill germs?

(j) When a peeled apple is left exposed to the air it begins to turn brown. This is because one of the substances in the apple is being oxidised. What is the oxidising agent?

(k) Sulfur dioxide is commonly used as a food preservative. How does it act as a food preservative?

(l) Explain the term *redox reaction*.

(m) Is combustion an oxidation or a reduction reaction? Explain your answer.

Chapter review questions

14.2 In the following examples indicate clearly, by showing electron loss or gain, which species is being oxidised and which is being reduced.

Show the oxidising and reducing agents in each of the reactions.

(a) $2Ca + O_2 \rightarrow 2CaO$

(b) $2K + Br_2 \rightarrow 2KBr$

(c) $Zn + I_2 \rightarrow ZnI_2$

(d) $2Cu + S \rightarrow Cu_2S$

(e) $2Fe^{2+} + Cl_2 \rightarrow 2Fe^{3+} + 2Cl^-$

(f) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

(g) $Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$

(h) $2Br^- + Cl_2 \rightarrow Br_2 + 2Cl^-$

14.3 Write down the oxidation number of each element in each of the following: I_2, KCl, MgF_2, H_2SO_4, H_2O_2, $CaCO_3$, Fe, H_2S, IO^-, IO_3^-, PCl_5, $NiSO_4$, CS_2, MgH_2, $Fe_2(SO_4)_3$.

14.4 Write down the oxidation number of Mn in each of the following compounds: $MnSO_4$, Mn_2O_3, MnO_2, $KMnO_4$.

14.5 **(a)** Define oxidation number. What is the oxidation number of chromium in the following: (i) $HCrO_4^-$, (ii) Cr_2O_3, (iii) $Cr_2O_7^{2-}$?

(b) What is the oxidation number of oxygen in OF_2? Explain why the oxidation number you have given is assigned to oxygen in this case.

[LCH]

14.6 Use oxidation numbers to determine whether or not each of the following is an oxidation–reduction reaction and if so, state which species is being oxidised and which is being reduced.

(a) $H_2SO_3 + OH^- \rightarrow HSO_3^- + H_2O$

(b) $Cu_2O + 2H^+ \rightarrow Cu + Cu^{2+} + H_2O$

(c) $3Ag + 4H^+ + NO_3^- \rightarrow 3Ag^+ + NO + 2H_2O$

[LCH]

14.7 In the case of the following reactions, indicate clearly by showing the changes in the oxidation numbers, which species is being oxidised and which is being reduced.

(a) $2HgCl_2 + SnCl_2 \rightarrow Hg_2Cl_2 + SnCl_4$

(b) $NH_4NO_3 \rightarrow N_2O + 2H_2O$

(c) $3Cl_2 + 6OH^- \rightarrow 5Cl^- + ClO_3^- + 3H_2O$ [LCH]

14.8 Using oxidation numbers, balance each of the following equations:

(a) $MnO_4^- + H_2S + H^+ \rightarrow Mn^{2+} + S + H_2O$ [LCH]

(b) $Cr_2O_7^{2-} + Cl^- + H^+ \rightarrow Cr^{3+} + H_2O + Cl_2$ [LCH]

(c) $Zn + NO_3^- + H^+ \rightarrow Zn^{2+} + N_2H_4 + H_2O$ [LCH]

(d) $MnO_4^- + H^+ + Cl^- \rightarrow Mn^{2+} + Cl_2 + H_2O$ [LCH]

(e) $ClO_3^- + I^- + H^+ \rightarrow I_2 + Cl^- + H_2O$ [LCH]

(f) $MnO_4^- + I^- + H^+ \rightarrow Mn^{2+} + H_2O + I_2$ [LCH]

(g) $Cr_2O_7^{2-} + H^+ + S \rightarrow SO_2 + OH^- + Cr_2O_3$ [LCH]

(h) $HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + H_2O$

(i) $KMnO_4 + H_2O_2 + H_2SO_4 \rightarrow MnSO_4 + O_2 + K_2SO_4 + H_2O$

(j) $KMnO_4 + SO_2 + H_2O \rightarrow MnO_2 + K_2SO_4 + H_2SO_4$

(k) $Na_2S_2O_3 + Br_2 \rightarrow NaBr + Na_2S_4O_6$

(l) $Na_2S_2O_3 + H_2O_2 + H_2SO_4 \rightarrow Na_2SO_4 + S + H_2O$

14.9 A solution of chlorine in water is added to a solution of potassium iodide, KI. It is observed that the colourless solution of KI turns a purple colour, Figure 14.14. The following reaction occurs:

$Cl_2 + KI \rightarrow I_2 + 2KCl$

(a) Identify the species that is oxidised.

(b) Identify the species that is reduced.

(c) What is the oxidising agent?

(d) What is the reducing agent?

(e) Assign oxidation numbers to each element in the above equation and hence write the balanced chemical equation for the reaction.

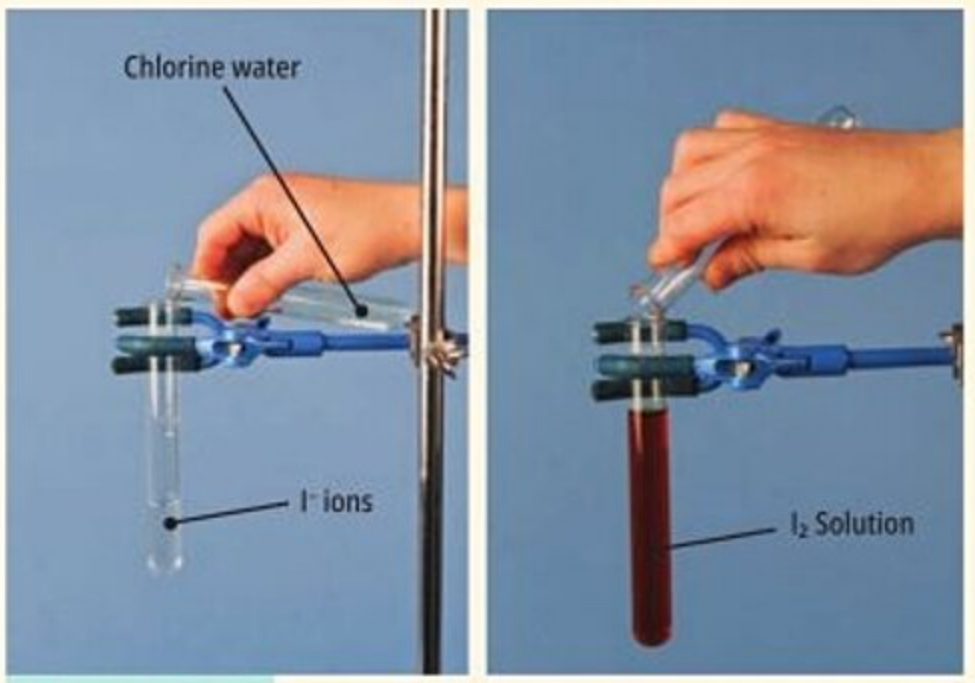
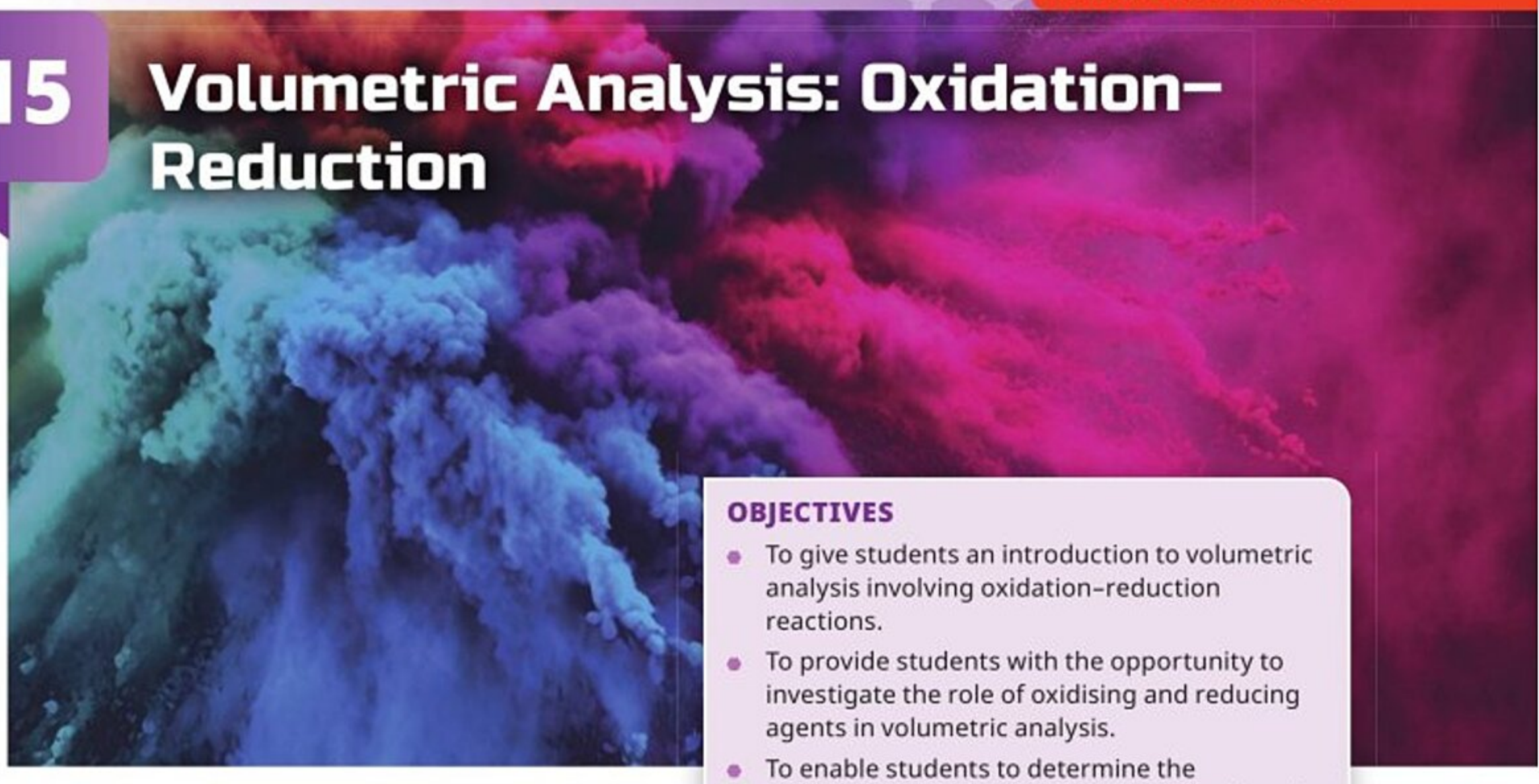


Figure 14.14

15 Volumetric Analysis: Oxidation–Reduction



OBJECTIVES

- To give students an introduction to volumetric analysis involving oxidation–reduction reactions.
- To provide students with the opportunity to investigate the role of oxidising and reducing agents in volumetric analysis.
- To enable students to determine the concentrations of substances being analysed in volumetric analysis involving oxidation-reduction reactions.

15.1 Introduction

In Chapters 12 and 13, we studied how volumetric analysis could be used to determine the concentrations of solutions of acids and bases. In Chapter 14, we saw that many reactions in chemistry may be classified as oxidation–reduction reactions. In this chapter, we will study how volumetric analysis may be used to determine the concentrations of oxidising and reducing agents.

The most important oxidising agent that we will come across in this course is **potassium permanganate**, which has the formula **$KMnO_4$**, Figure 15.1. It is a strong oxidising agent and one of its uses is to remove iron ions from water. It oxidises soluble Fe^{2+} ions to insoluble Fe^{3+} ions which can then be filtered out of the water. It need only be present in very dilute concentrations (1 – 3 p.p.m). Therefore, the purple colour of the permanganate is not visible in the water. It is also used in dilute solutions in medicine as an antiseptic to treat fungal infections.

The more modern ('systematic') name for potassium permanganate is **potassium manganate(VII)** and you will see this name commonly used on Leaving Certificate exam papers. Since the name 'potassium permanganate' is so well known, we will use both terms throughout this chapter and in subsequent chapters.

Figure 15.1 Potassium permanganate is used to remove excess iron from water.

Before studying redox titrations, it is important to be familiar with some key points regarding potassium permanganate [potassium manganate(VII)]. These points will be studied in the next section.

15.2 Potassium permanganate [potassium manganate(VII)]: oxidising agent

The main points about potassium permanganate [potassium manganate(VII)] may be summarised as follows:

- Potassium permanganate is a purple-coloured solid.
- It is not a primary standard, as it cannot be obtained in a state of very high purity.
- It is unstable and decomposes in the presence of sunlight and heat.
- Therefore, the concentrations of potassium permanganate [potassium manganate(VII)] solutions vary over time.
- As a result of this, solutions of potassium permanganate must be standardised by titration against a primary standard solution.
- Potassium permanganate acts as an oxidising agent by gaining five electrons in acidic solution. The following is the reaction that takes place in acidic solution:

$$\underset{\text{purple}}{MnO_4^-} + 8H^+ + 5e^- \rightarrow \underset{\text{colourless}}{Mn^{2+}} + 4H_2O$$

The above reaction is illustrated in Figure 15.2.

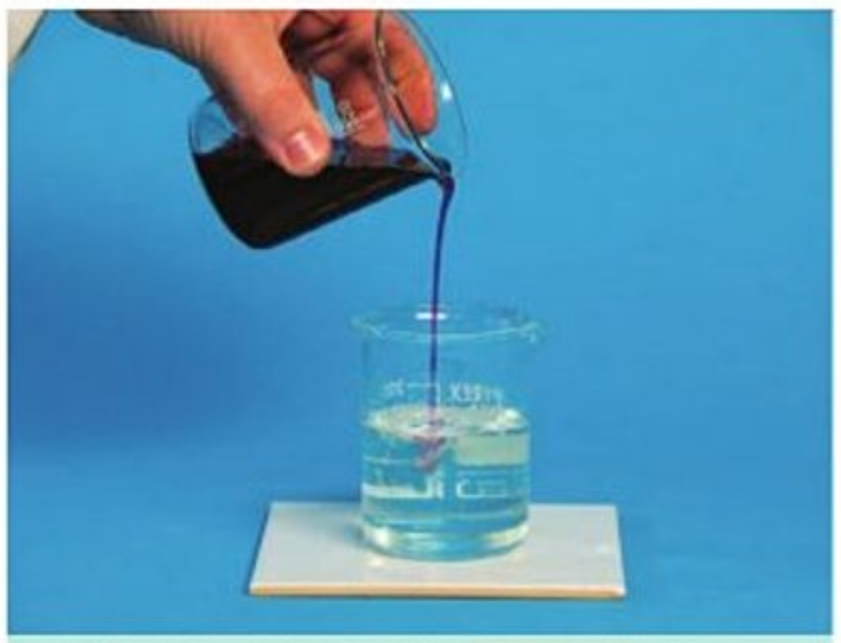


Figure 15.2 As the acidified potassium permanganate solution is being added to the reducing agent, the manganese changes from an oxidation state of +7 (purple) to an oxidation state of +2 (colourless).

As a general rule, when dealing with redox reactions, the transfer of electrons is emphasised by writing the half-reactions rather than the fully balanced equations. The above half-reaction is so important and occurs so frequently in this course that it is recommended that you learn it off by heart.

- In order to get the permanganate to undergo the above reaction, it is necessary to add some dilute acid to supply the H^+ ions.
- When acidifying $KMnO_4$ solution, it is usual to use **sulfuric acid**. If HCl were used, the Cl^- ions would be oxidised to Cl_2 by the $KMnO_4$. If nitric acid were used, it could interfere with the reaction, as nitric acid is itself a strong oxidising agent.
- In neutral or basic solution, the above reaction does not take place, i.e. the manganese ion does not change from an oxidation state of +7 (purple) to +2 (colourless). Instead, the manganese ion changes from the oxidation state of +7 (purple) to + 4 (brown).
- This oxidation state appears as a **brown solid precipitate** and is due to the formation of manganese dioxide, MnO_2, Figure 15.3. The manganese dioxide is formed according to the reaction:

$$\underset{\text{purple}}{MnO_4^-} + 2H_2O + 3e^- \rightarrow \underset{\text{brown}}{MnO_2\downarrow} + 4OH^-$$

Figure 15.3 When the permanganate ion reacts with a reducing agent in neutral or basic solution, the manganese atom changes from an oxidation state of +7 (purple) to an oxidation state of +4 (brown).

- Potassium permanganate [potassium manganate(VII)] acts as its own indicator. It is said to be **self-indicating**. As explained above, it changes colour from purple to colourless when acting as an oxidising agent in acidic solution. This colour change enables us to detect the end point. (This will be explained in more detail later in this chapter.)
- Because of the intense purple colour of potassium permanganate solution, the bottom of the meniscus can be difficult to see. Therefore, it is usual to **read the top of the meniscus**, rather than the bottom of the meniscus, Figure 15.4.
- Because of the intense purple colour, its fairly low solubility and the fact that it is a good oxidising agent, we usually use fairly dilute solutions of $KMnO_4$ in redox titrations. For example, 0.02 M solutions will frequently be used in the redox titrations on this course.

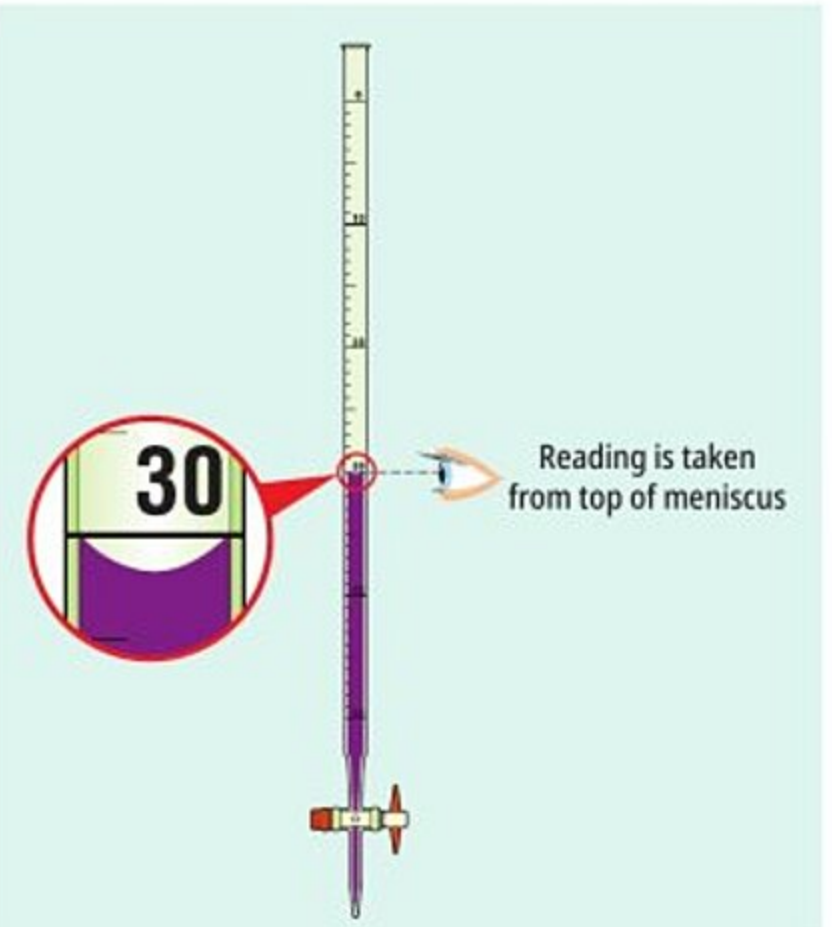


Figure 15.4 In the case of potassium permanganate solutions, it is normal to take the readings from the top of the meniscus.

In the Leaving Certificate Chemistry course, we are required to study two examples of redox titrations. The first of these is the reaction between MnO_4^- and Fe^{2+} ions.

15.3 The reaction of MnO_4^- and Fe^{2+} ions

As already stated, it is not possible to make up a solution of $KMnO_4$ to an accurately known concentration by simply weighing out a certain amount of the solid and dissolving it in a known volume of solution. This is because $KMnO_4$ is not a primary standard.

- However, it is possible to determine the concentration of a $KMnO_4$ solution by titrating it against a solution containing Fe^{2+} ions.
- $KMnO_4$ is an oxidising agent and, when added to a solution containing Fe^{2+} ions (reducing agent), it converts the Fe^{2+} ions to Fe^{3+} ions.

  This is shown in the following half equations:

  Oxidising agent: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$ (a)

  Reducing agent: $Fe^{2+} \rightarrow Fe^{3+} + e^-$ (b)

- If we examine equation (a) above, we see that each MnO_4^- ion can accept **five** electrons. However, each Fe^{2+} ion can lose only **one** electron.
- Therefore, five Fe^{2+} ions will be required to react with one MnO_4^- ion, i.e. the ions react in the ratio of one MnO_4^- ion to five Fe^{2+} ions. Think carefully about this.
- To balance the electron transfer, we can write the above two equations as follows:

  Oxidising agent: $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$

  Reducing agent: $5Fe^{2+} \rightarrow 5Fe^{3+} + 5e^-$

  Adding: $MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

The important point to note from this equation is that **MnO_4^- ions react with Fe^{2+} ions in the ratio of 1 : 5.** (We have already used this idea in the last chapter to balance redox equations). You will need to know this ratio for subsequent calculations.

We now consider some important points about the Fe^{2+} reducing agent in the reactions represented by the above equations:

- You might think that Fe^{2+} ions for the titration would be obtained by dissolving crystals of iron(II) sulfate, $FeSO_4.7H_2O$ in water.
- However, it is not possible to use this compound as a primary standard because (i) the crystals tend to be oxidised slightly by the air and (ii) the crystals tend to lose their water of crystallisation when exposed to the air. The spontaneous loss of water of crystallisation to the air is known as *efflorescence*.

Efflorescence is the spontaneous loss of water of crystallisation from a hydrated crystalline salt.

The word 'spontaneous' means it occurs on its own or naturally without any external intervention (e.g. heating) being necessary. Other examples of compounds that undergo efflorescence are $CuSO_4.5H_2O$ and $Na_2CO_3.10H_2O$.

A substance is said to be **hygroscopic** if it has the ability to spontaneously absorb moisture from the surrounding air without dissolving into a liquid solution.

Examples of hygroscopic compounds are iron(II) sulfate, $FeSO_4$, silica gel, SiO_2 (used in packaging to absorb moisture) and concentrated sulfuric acid.

Deliquescence is the spontaneous process by which a substance absorbs moisture from the atmosphere to the extent that it dissolves into a liquid solution.

Examples of deliquescent compounds are sodium hydroxide and potassium hydroxide.

- The anhydrous compound $FeSO_4$ cannot be used either because it takes in moisture from the air, i.e. it is hygroscopic.
- Instead of using **iron(II) sulfate**, we use a substance called **ammonium iron(II) sulfate** as a source of Fe^{2+} ions. This can be obtained in a high degree of purity, is not affected by the air, and so it can be used as a primary standard, Figure 15.5.
- The formula of ammonium iron(II) sulfate is $(NH_4)_2SO_4.FeSO_4.6H_2O$. This is referred to as a 'double salt'. A **double salt** is a salt that consists of two different simple salts crystallised together in a fixed ratio within the same crystal structure.
- To remember its formula, write down the formula of iron(II) sulfate and put the formula of ammonium sulfate in front of it.
- The old name for ammonium iron(II) sulfate was 'ferrous ammonium sulfate'. This name is still widely used and is probably the name that appears on the container of the salt in the chemical store of your school.
- Even though ammonium iron(II) sulfate is hydrated, it is still used as a primary standard because it is very stable and does not spontaneously lose its water of crystallisation to the air.
- The high relative molecular mass of ammonium iron(II) sulfate (392.17) ensures that percentage errors due to slight inaccuracies in weighing will be reduced.
- When making up a solution of ammonium iron(II) sulfate, it is important that it is dissolved in water that contains dilute sulfuric acid. **The sulfuric acid prevents the Fe^{2+} ions being oxidised to Fe^{3+} ions by the oxygen in the air**. Fe^{2+} ions are more stable in the acidic solution and this makes them less likely to react with oxygen.

EXAM TIP!

Make sure that you can explain the role of the dilute sulfuric acid, as it could be asked on an exam paper!

Figure 15.5 The formula of ammonium iron(II) sulfate is $(NH_4)_2SO_4.FeSO_4.6H_2O$. It can be used as a primary standard.

15.1 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 11 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 11

To prepare a standard solution of ammonium iron(II) sulfate and to use this solution to standardise a solution of potassium permanganate [potassium manganate(VII)] by titration

Introduction

In this experiment, we will make up a standard solution of ammonium iron(II) sulfate. We will then use this standard solution to find out the exact concentration of a solution of potassium permanganate by titration.

Key steps in procedure

- Some ammonium iron(II) sulfate is accurately weighed out on a clock glass using the laboratory balance.
- Using a graduated cylinder, dilute sulfuric acid is added to a beaker containing some deionised water.
- The ammonium iron(II) sulfate is transferred to the beaker taking all the usual precautions outlined in Chapter 12.

Explanation

- The ammonium iron(II) sulfate is dissolved in dilute sulfuric acid as the sulfuric acid prevents the Fe^{2+} ions being oxidised to Fe^{3+} ions by the oxygen in the air.

Procedure (continued)

- The ammonium iron(II) sulfate solution is stirred to fully dissolve the crystals and, when dissolved, the solution is then transferred to a clean volumetric flask using a funnel.
- All the washings are transferred to the volumetric flask. The bottom of the meniscus of the solution is brought up to the mark with deionised water.
- The stoppered flask is inverted about 20 times.
- The pipette, burette and conical flask are washed with deionised water.
- The burette is washed with some of the potassium permanganate solution and filled with the aid of a funnel, Figure 15.6. The funnel is removed.
- The top of the meniscus of the potassium permanganate solution is adjusted so that it is level with the zero mark of the burette, taking the reading at eye level.
- A check is made to ensure that the tap and the space below the tap are also filled with the permanganate solution.
- Some of the ammonium iron(II) sulfate solution is transferred to a clean, dry beaker and the pipette is washed out with this solution.

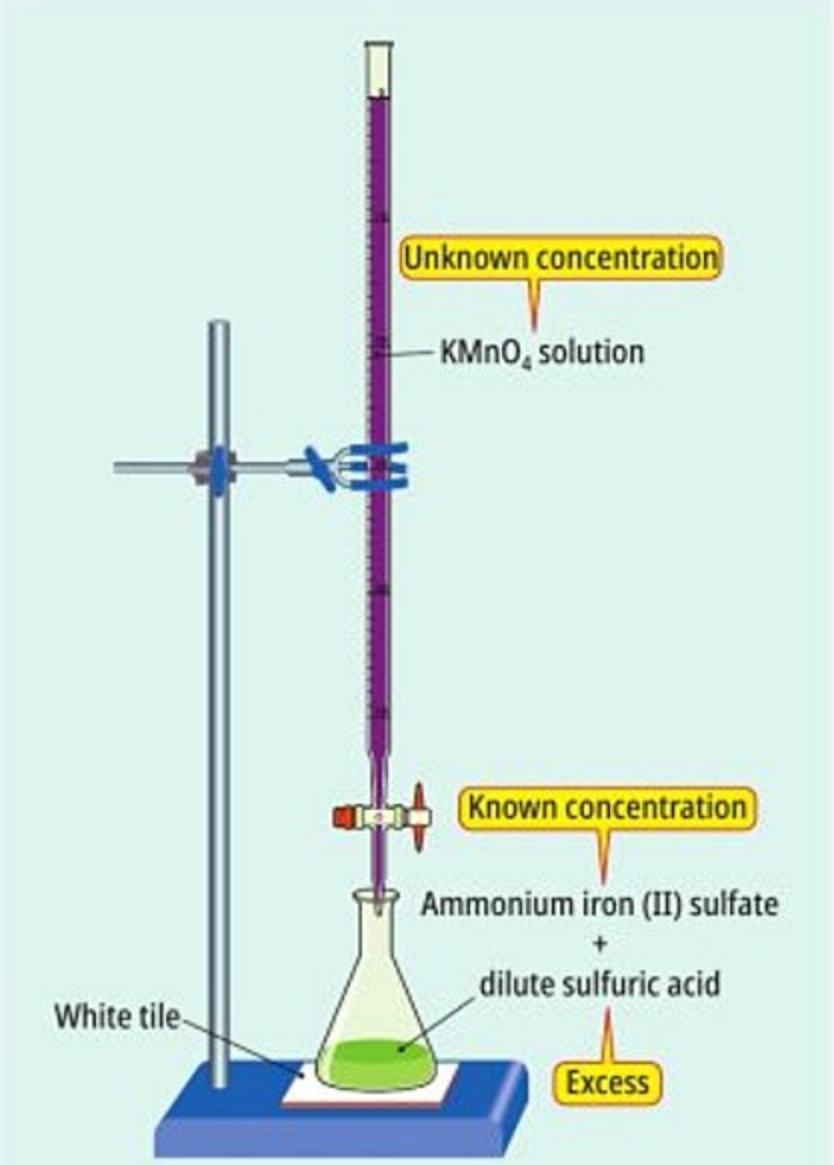


Figure 15.6 Titration of potassium permanganate [potassium manganate(VII)] solution against a standard solution of ammonium iron(II) sulfate.

- Using a pipette filler, the pipette is filled to the mark with the ammonium iron(II) sulfate solution and this amount of ammonium iron(II) sulfate is placed in the conical flask.
- Using a graduated cylinder, some dilute sulfuric acid is added to the conical flask. The sulfuric acid should be in excess.

Explanation

- The need for an excess of sulfuric acid is to ensure that a sufficient supply of H^+ ions is present so that all of the MnO_4^- ions are reduced to Mn^{2+} ions according to the following half equation:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

If no acid (or insufficient acid) is added, a brown precipitate of MnO_2 will be formed in the conical flask during the titration.

Procedure (continued)

- The titration is carried out in the usual manner until a faint permanent pink colour is observed at the end point.

Explanation

- The faint permanent pink colour at the end point may be explained as follows: as long as Fe^{2+} ions are present in the conical flask, the $KMnO_4$ solution that is run into the flask loses it colour. When all the Fe^{2+} ions have reacted, the next drop of $KMnO_4$ solution gives a permanent pink colour. Therefore, at the end point, one single drop of $KMnO_4$ from the burette will turn the solution in the conical flask a faint pink colour. The $KMnO_4$ is acting as its own indicator.

Procedure (continued)

- One rough and two accurate titrations are carried out. The two accurate titration figures should agree to within 0.1 cm^3.
- As $KMnO_4$ stains glassware, all glassware must be thoroughly washed out when all titrations are completed.

Calculations

The exact concentration of the $KMnO_4$ solution may be calculated using the average titration figure. The method of calculation is shown in Example 15.1.

You may have noticed that the first few drops of $KMnO_4$ added to the conical flask are decolorised slowly but subsequent drops are decolorised more rapidly. This is due to an occurrence called **autocatalysis** (Chapter 17). The reaction is catalysed by the Mn^{2+} ions formed in the reaction. As soon as the Mn^{2+} ions are formed, the rate of the reaction increases as the Mn^{2+} ions are produced.

DIGITAL: A video of this experiment is available on FolensHIVE.

15.4 Solving volumetric problems in redox reactions

The general expression derived for solving volumetric problems involving acid–base reactions may also be used for solving volumetric problems involving redox reactions. (The derivation of this formula is the same as outlined for acid–base reactions.)

For redox reactions we write this expression as follows:

V_o = volume of oxidising agent (cm^3)

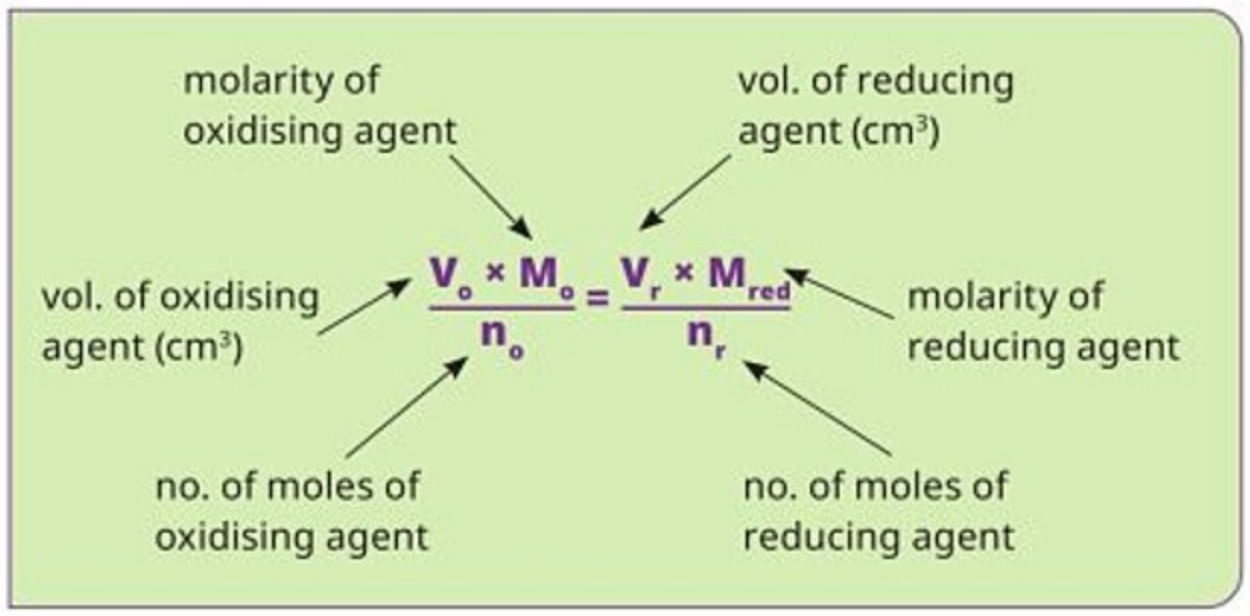
M_o = molarity of oxidising agent

n_o = number of moles of oxidising agent (from balanced equation)

V_r = volume of reducing agent (cm^3)

M_{red} = molarity of reducing agent

n_r = number of moles of reducing agent (from balanced equation)


molarity of oxidising agent
vol. of reducing agent (cm³)
vol. of oxidising agent (cm³)
$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$
molarity of reducing agent
no. of moles of oxidising agent
no. of moles of reducing agent

The use of this equation is illustrated in the following examples.

Example 15.1

Question

A student made up a 0.12 M ammonium iron(II) sulfate solution and used this to standardise a solution of potassium permanganate [potassium manganate(VII)]. 25 cm^3 of the ammonium iron(II) sulfate solution were titrated against the potassium permanganate solution. The equation for the reaction is:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The average titration figure was 23.75 cm^3. Calculate the concentration of the potassium permanganate solution in (a) moles per litre and (b) grams per litre.

Answer

Step 1

Calculate the molarity of the $KMnO_4$ solution (oxidising agent)

From the balanced equation, we see that one mole of MnO_4^- reacts with 5 moles of Fe^{2+}, i.e. $n_o = 1$ and $n_r = 5$.

MnO_4^- Fe^{2+}

Given:

$V_o = 23.75$

$M_o = ?$

$n_o = 1$

$V_r = 25$

$M_{red} = 0.12$

$n_r = 5$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

$$\frac{23.75 \times M_o}{1} = \frac{25 \times 0.12}{5}$$

$$M_o = \frac{25 \times 0.12}{5 \times 23.75}$$

$= 0.0253$ moles per litre. (a)

K	= 39.1
Mn	= 54.94
$4 \times O = 4 \times 16$	= 64.00
$M_r\ KMnO_4$	= 158.04

Step 2

Convert to g/L $= 0.0253 \times 158.04$ grams per litre (Rel. molecular mass $KMnO_4 = 158.04$)

$= 3.998$ g/L. (b)

Answer: Concentration of $KMnO_4$ solution is (a) 0.0253 moles per litre, (b) 3.998 grams per litre.

Example 15.2

Question

A sample of iron(II) sulfate crystals $FeSO_4.xH_2O$ was analysed in order to find out the value of x. 6.42 g of the crystals were dissolved in deionised water to which some dilute sulfuric acid had been added, and the resulting solution was made up to 250 cm^3 in a volumetric flask. 25 cm^3 samples of this solution were titrated against 0.018 M $KMnO_4$ solution. The balanced equation for the reaction is:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

The average titration figure was 25.5 cm^3. Calculate the value of x in the above formula.

Answer

When solving problems of this type, proceed as we did in the case of acid–base volumetric problems. First calculate the concentration of the iron(II) sulfate solution in moles per litre. Then relate this number of moles to the mass of substance dissolved and hence calculate the relative molecular mass of the hydrated salt. Once this is known, it is easy to calculate the value of x.

Step 1

Calculate the molarity of the $FeSO_4$ solution (reducing agent)

MnO_4^- Fe^{2+}

Given:

$V_o = 25.5$

$M_o = 0.018$

$n_o = 1$

$V_r = 25$

$M_{red} = ?$

$n_r = 5$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

$$\frac{25.5 \times 0.018}{1} = \frac{25 \times M_{red}}{5}$$

$$M_{red} = \frac{25.5 \times 0.018 \times 5}{25}$$

$= 0.0918$ moles/litre $FeSO_4$

$= 0.023$ moles/250 cm^3 $FeSO_4$

i.e. by dissolving 6.42 g of the crystals in 250 cm^3 of solution, we obtain a solution which contains 0.023 moles.

Step 2

Calculate the relative molecular mass of $FeSO_4.xH_2O$

From Step 1, 0.023 moles $FeSO_4.xH_2O$ = 6.42 g

1 mole $FeSO_4.xH_2O = \frac{6.42}{0.023}$ g = 279.13 g

1 mole $FeSO_4.xH_2O$ = 279.13 g

Step 3

Calculate the value of x using the values of M_r of $FeSO_4$ and M_r of $FeSO_4.xH_2O$

$$151.92 + 18x = 279.13$$

$$18x = 279.13 - 151.92 = 127.21$$

$$x = \frac{127.21}{18} = 7$$

Answer: x = 7. The formula is $FeSO_4.7H_2O$

Fe	= 55.85
S	= 32.07
4 × O = 4 × 16	= 64
Mr $FeSO_4$	= 151.92

TEST YOURSELF: Attempt Questions 15.1–15.7 and W15.1–W15.6.

Iron deficiency in our bodies

Our bodies can easily become deficient in iron. This is particularly true for young teenagers who are growing rapidly. Iron deficiency (also called anaemia) is usually remedied with a course of iron tablets and/or a change in diet. Some foods such as liver, kidney, egg yolk and green leafy vegetables are rich in iron, Figure 15.7. Iron is stored in the form of various iron compounds in these foods. Some processed foods such as cereals are commonly fortified with iron – usually in the form of iron salts.

Figure 15.7 Many foods contain iron stored in the form of various iron compounds.

Iron is an important element in our bodies because it is part of the haemoglobin molecule in our blood. Haemoglobin is the molecule that is responsible for the transport of oxygen in our blood. The oxygen actually becomes attached to the iron part of the haemoglobin molecule, Figure 15.8.

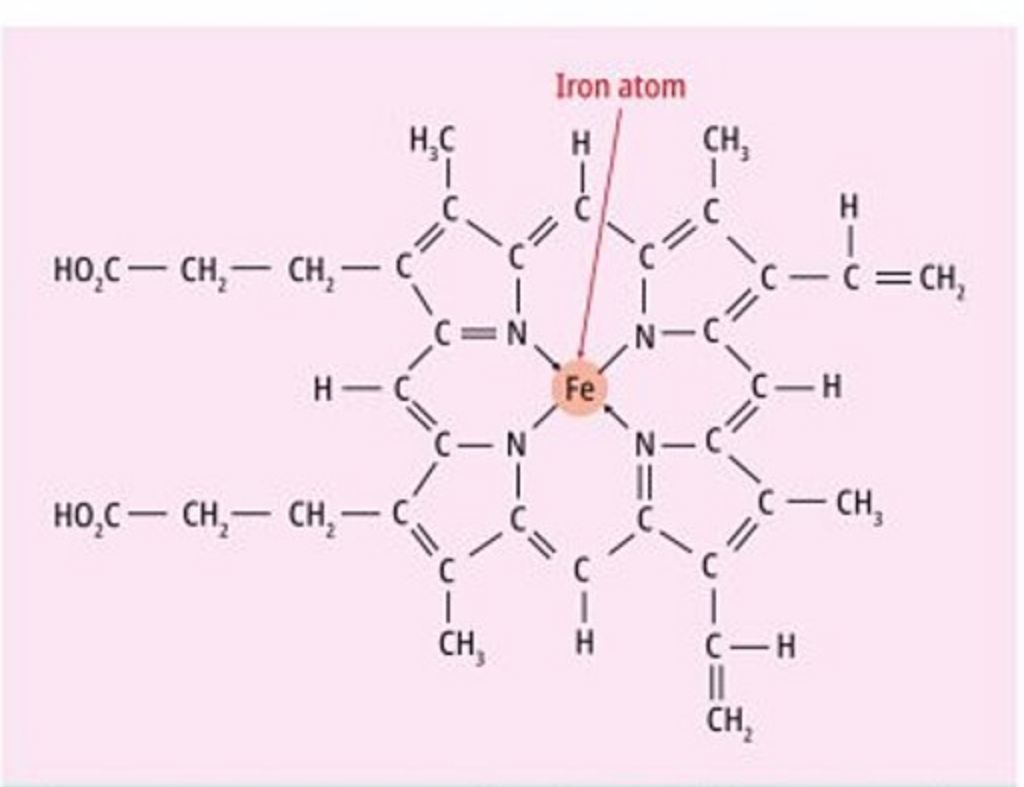


Figure 15.8 Iron is part of the haemoglobin molecule in our blood.

You are not expected to remember the structure of the haemoglobin molecule!

Since anaemia is caused by a shortage of haemoglobin in the blood, people suffering from anaemia are often prescribed 'iron tablets', Figure 15.9. These tablets usually contain anhydrous iron(II) sulfate, $FeSO_4$. In Experiment 15.2 we will carry out an experiment to find the actual quantity of iron(II) sulfate in the tablets.

Figure 15.9 Iron tablets usually contain anhydrous iron(II) sulfate, $FeSO_4$.

15.2 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 12 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 12

To determine the percentage of elemental iron in an iron tablet

Introduction

In this experiment, we will measure the amount of iron(II) sulfate, $FeSO_4$, in an iron tablet and then compare our result with the quantity stated on the packet. The quantity on the packet is usually stated in terms of milligrams of the anhydrous salt, e.g. 200 mg $FeSO_4$ per tablet.

The amount of iron(II) sulfate is measured by dissolving some tablets in dilute sulfuric acid and titrating the solution against standardised potassium permanganate [potassium manganate(VII)] solution. The potassium permanganate must be standardised immediately before use in this titration since, as already mentioned, $KMnO_4$ is unstable and is decomposed by the presence of light and heat, i.e. the concentration of the solution varies over time.

Key steps in procedure

- Five tablets are placed on a clock glass and the total mass found using the laboratory balance. If the iron tablets are in the form of capsules, the contents of five capsules are emptied onto the clock glass and the total mass of the contents is found.
- The tablets are ground up using a mortar and pestle. This helps the iron sulfate to dissolve more quickly. Some dilute sulfuric acid is added to the mortar to make it easier to grind the tablets.
- Taking all the precautions outlined previously, the paste of acid and tablets is transferred to a beaker containing some dilute sulfuric acid.
- The solution is stirred to dissolve the iron sulfate in the paste.

Observation

- It may be observed that the solution is cloudy rather than clear.

Explanation

- The outer coating of the tablets may not dissolve easily and this may give a cloudy appearance to the solution. Do not worry about this as it will not affect your results. (Iron tablets often have a coating to slow down the rate at which they dissolve in the stomach. This reduces the chance of stomach upsets.)

Procedure (continued)

- Taking all the precautions outlined in previous experiments, the solution of the tablets is transferred to a clean volumetric flask. The bottom of the meniscus of the solution is brought up to the mark with deionised water.
- The stoppered flask is inverted about 20 times.
- The pipette, burette and conical flask are rinsed with deionised water.
- The burette is washed with some of the potassium permanganate solution and filled with the aid of a funnel, Figure 15.10. The funnel is removed.
- The top of the meniscus of the potassium permanganate solution is adjusted so that it is level with the zero mark of the burette.
- A check is made to ensure that the tap and the space below the tap are filled with the permanganate solution.
- Some of the iron tablet solution is transferred from the volumetric flask to a clean, dry beaker. Using a pipette filler, the pipette is washed out with a small amount of this solution. The pipette is then filled to the mark with the iron tablet solution and this volume is pipetted into the conical flask.
- Using a graduated cylinder, dilute sulfuric acid is added in excess to the conical flask (for the same reason as stated in the previous experiment).
- A titration is carried out in the usual way until a faint permanent pink colour is observed at the end point. One rough and two accurate titrations are carried out.

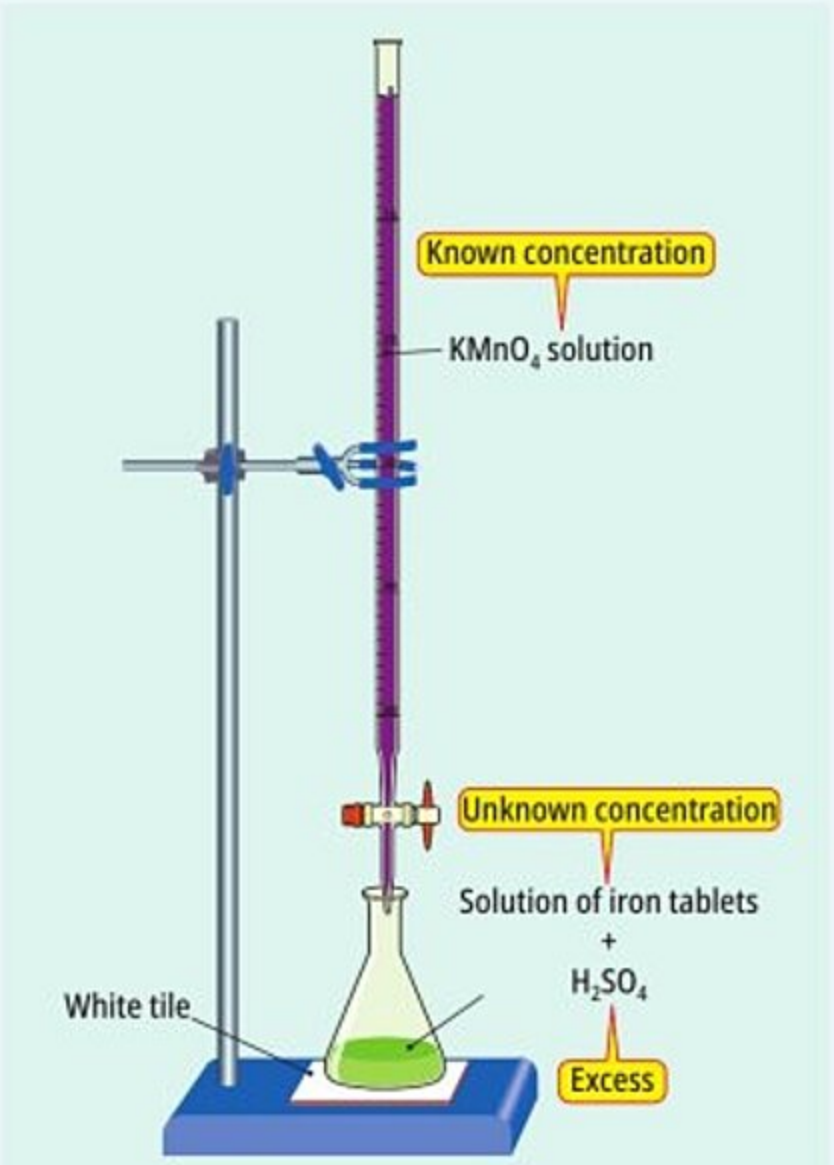


Figure 15.10 Determining the percentage of elemental iron in iron tablets.

Calculations

Using the average titration figure, the mass of iron in each tablet is calculated. The method of calculating is shown in Example 15.3.

DIGITAL: A video of this experiment is available on FolensHIVE.

Example 15.3

Question

A student was asked to analyse an iron tablet to determine if the amount of iron sulfate per tablet stated on the packet was correct. He dissolved five tablets whose total mass was 1.21 grams in dilute sulfuric acid and made the solution up to 250 cm^3 in a volumetric flask. He then titrated 25 cm^3 portions of the resulting solution against 0.015 M potassium permanganate [potassium manganate(VII)]. The average titration figure was 5.75 cm^3. Calculate (a) the mass of anhydrous $FeSO_4$ in each tablet, (b) the mass of elemental iron in each tablet, (c) the percentage of $FeSO_4$ in each tablet and (d) the percentage of elemental iron in each tablet.

The equation for the reaction is:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Answer

Step 1

Calculate the molarity of the $FeSO_4$ solution.

From the balanced equation, we see that one mole of MnO_4^- reacts with five moles of Fe^{2+}, i.e. $n_o = 1$ and $n_r = 5$.

MnO_4^- Fe^{2+}

Given:

$V_o = 5.75$

$M_o = 0.015$

$n_o = 1$

$V_r = 25$

$M_{red} = ?$

$n_r = 5$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

$$\frac{5.75 \times 0.015}{1} = \frac{25 \times M_{red}}{5}$$

$$M_{red} = \frac{5.75 \times 0.015 \times 5}{25}$$

$= 0.0173$ moles per litre

Step 2

Convert to g/L

$= 0.0173 \times 151.92$ g/L (Rel. molecular mass $FeSO_4 = 151.92$)

$= 2.628$ g/L.

Fe	= 55.85
S	= 32.07
$4 \times O = 4 \times 16 = 64$	
$M_r FeSO_4$	= 151.92

Step 3

Calculate the mass of $FeSO_4$ per 250 cm^3.

From Step 2, in the 250 cm^3 volumetric flask there are $\frac{2.628}{4} = 0.657$ grams of $FeSO_4$.

Step 4

Calculate the mass of $FeSO_4$ per tablet.

Thus, since we used 5 tablets, 1 tablet contains $\frac{0.657}{5}$ grams of $FeSO_4 = 0.131$ grams (a)

Step 5

Calculate the percentage of iron in $FeSO_4$.

The percentage of iron in $FeSO_4$ is $\frac{55.85}{151.92} \times 100 = 36.76\%$

Step 6

Calculate the percentage of $FeSO_4$ and Fe per tablet.

Therefore, the mass of iron in each tablet is 36.76% of 0.131 g = 0.048 g (b)

Mass of one tablet = $\frac{1.21}{5}$ = 0.242 g

% $FeSO_4$ in each tablet = $\frac{\text{Mass of } FeSO_4 \text{ per table}}{\text{Mass of one tablet}} = \frac{0.131}{0.242} \times 100 = 54.13\%$ (c)

% Fe in each tablet = $\frac{\text{Mass of Fe per table}}{\text{Mass of one tablet}} = \frac{0.048}{0.242} \times 100 = 19.83\%$ (d)

Answer: (a) 0.131 g FeSO4 (b) 0.048 g Fe (c) 54.13% FeSO4 (d) 19.83% Fe

SEC exam question

Question

A student carried out an experiment to investigate the percentage of elemental iron in tablets containing iron compounds. The student was given five of the tablets.

Describe how the student could use the tablets to make up an exact volume of a solution of iron(II). Your answer should identify all relevant chemicals and apparatus and describe how they were used.

Answer

The main steps including references to chemicals and apparatus are:

1. The five tablets are placed on a clock glass and the total mass found using the laboratory balance.
2. The tablets are ground up using a mortar and pestle.
3. Some dilute sulfuric acid is added to the mortar to make it easier to grind the tablets.
4. Using a graduated cylinder, add dilute sulfuric acid to a beaker.
5. The paste of acid and tablets is transferred from the mortar to the beaker containing the dilute sulfuric acid.
6. The mortar is rinsed out with deionised water and the rinsings are added to the beaker.
7. The solution is stirred with a glass rod to dissolve the iron sulfate in the paste.
8. Using a funnel, the solution of the tablets is transferred to a clean volumetric flask.
9. The beaker is rinsed out with deionised water and the rinsings are added to the volumetric flask.
10. The glass rod and funnel are rinsed with deionised water and the rinsings are added to the volumetric flask.
11. The funnel is removed.
12. Using a dropper, the bottom of the meniscus of the solution is slowly brought up to the graduation mark with deionised water taking the reading at eye level.
13. The flask is stoppered.
14. The stoppered flask is inverted about 20 times.

EXAM TIP!

When describing this procedure, always remember the seven main stages involved in making up a solution as shown in Figure 12.13 (p.210) of this textbook. Describe at least these 7 main stages and include as much additional information as you can remember from carrying out the experiment. Drawing labelled diagrams will also assist you in remembering the steps.

TEST YOURSELF: Attempt Questions 15.8–15.9 and W15.7–W15.8.

15.5 The reaction of iodine and sodium thiosulfate

The second type of redox titration that we will study in this course is the reaction between iodine and sodium thiosulfate. Sodium thiosulfate, $Na_2S_2O_3$, is an important reducing agent used in chemistry, Figure 15.11.

For example, sometimes excess chlorine may be added when disinfecting swimming pools and sodium thiosulfate is used to reduce the excess chlorine to harmless chloride ions. It is also used in analysing the amount of certain substances dissolved in water (e.g. oxygen), for extracting gold, and as an antidote to cyanide poisoning.

Figure 15.11 Sodium thiosulfate helps reduce excessive amounts of chlorine in swimming pool water.

We will be meeting sodium thiosulfate on many occasions in this course. The following is a summary of some important points about it:

- Sodium thiosulfate is commonly found in the form of a colourless crystalline solid of formula $Na_2S_2O_3.5H_2O$ called sodium thiosulfate pentahydrate, Figure 15.12. The *pent* part of the name refers to the five molecules of water in the formula. (The water content of sodium thiosulfate crystals is variable but the pentahydrate is the most common one.) These water molecules are not chemically bonded to the sodium thiosulfate molecule but are trapped within the crystal structure. If sodium thiosulfate pentahydrate is heated, the water of crystallisation is lost and a white powder is formed. This white powder is anhydrous $Na_2S_2O_3$.
- The thiosulfate ion, $S_2O_3^{2-}$, has a structure similar to that of the sulfate ion, SO_4^{2-}, except that one of the oxygen atoms in the sulfate ion is replaced by a sulfur atom in the thiosulfate ion, Figure 15.13. (The prefix 'thio' means 'sulfur'.)
- Sodium thiosulfate is a reducing agent and reacts with iodine molecules, I_2, to convert them to iodide ions, I^-. The equation for the reaction is:

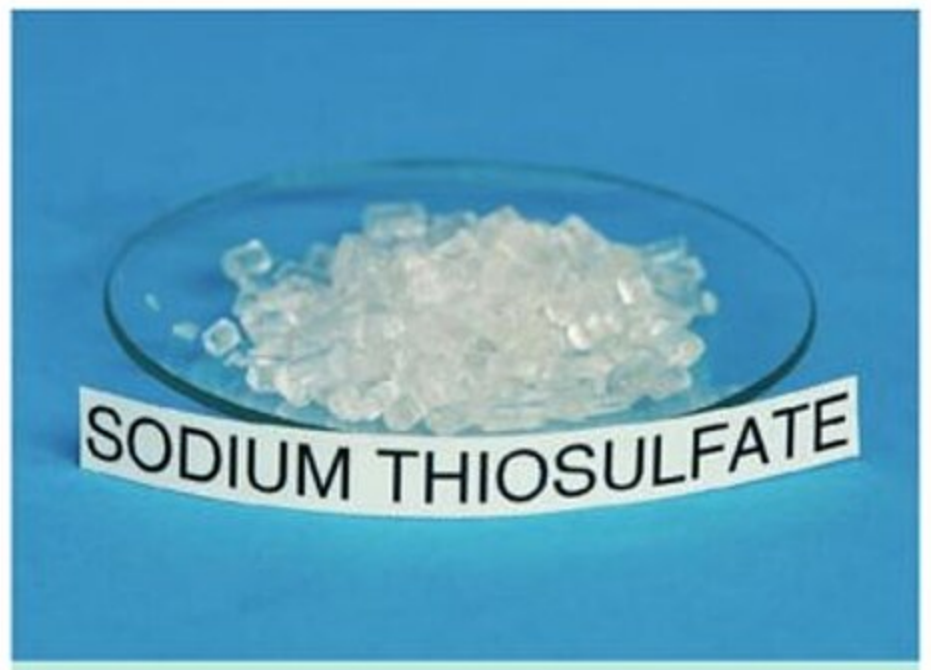


Figure 15.12 Sodium thiosulfate, $Na_2S_2O_3$, is one of the most useful reducing agents in chemistry. These crystals are hydrated and have the formula $Na_2S_2O_3.5H_2O$.

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

iodine + thiosulfate ion → tetrathionate ion + iodine ion

oxidising agent: I_2; reducing agent: $S_2O_3^{2-}$

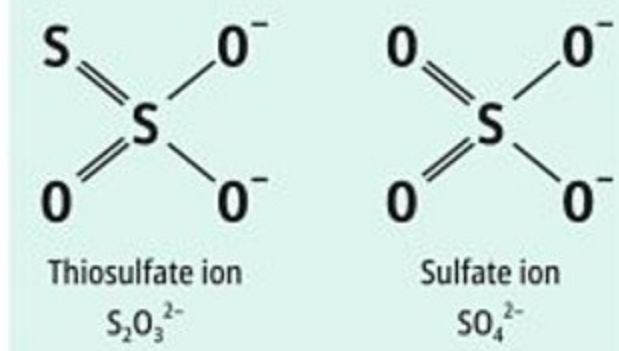


Figure 15.13 The thiosulfate and sulfate ions

- The $S_4O_6^{2-}$ ion formed in the above reaction is called the **tetrathionate ion**. Its structure may be represented as shown in Figure 15.14.

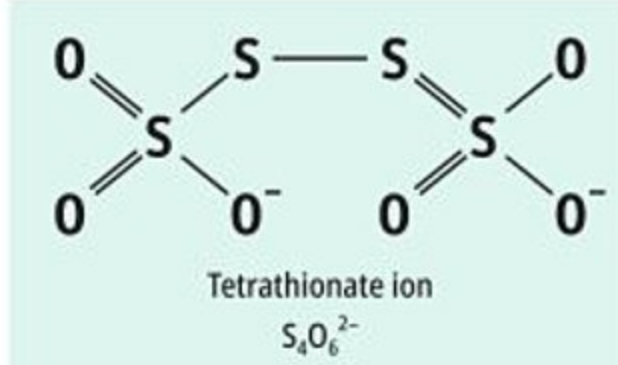


Figure 15.14 The tetrathionate ion, $S_4O_6^{2-}$.

Note that the thiosulfate ion (the reducing agent) is oxidised to the tetrathionate ion. This may be easily seen by assigning oxidation numbers.

$$\underset{+2}{I_2} + 2\underset{+2}{S_2O_3^{2-}} \rightarrow \underset{+2.5}{S_4O_6^{2-}} + 2\underset{}{I^-}$$

- Sodium thiosulfate is not a primary standard, as it cannot be obtained in a sufficiently pure state and the crystals are efflorescent. Therefore, a solution of known concentration cannot be made up by weighing out a certain amount of the solid and dissolving it in a known volume of solution. A sodium thiosulfate solution is standardised by titrating it against a standard iodine solution.
- A standard solution of iodine cannot be made up by direct weighing. This is because iodine slightly vaporises (sublimes – changes directly from solid to vapour) even at room temperature. In addition, iodine is almost completely insoluble in water. For these two reasons, iodine is not a primary standard.

How therefore do we make up a standard solution of iodine? Stay tuned!

- A standard solution of iodine is obtained by reacting a standard solution of potassium permanganate [potassium manganate(VII)] with excess potassium iodide solution. Consider the reaction of acidified permanganate ions with iodide ions:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O \quad \text{(a)}$$
$$2I^- \rightarrow I_2 + 2e^- \quad \text{(b)}$$

In equation (a) we see that five electrons are gained. In equation (b), two electrons are lost. We can balance the electron gain and loss by multiplying (a) by 2 and (b) by 5. This gives us:

$$\text{(a)} \times 2 \quad 2MnO_4^- + 16H^+ + 10e^- \rightarrow 2Mn^{2+} + 8H_2O$$
$$\text{(b)} \times 5 \quad 10I^- \rightarrow 5I_2 + 10e^-$$

Adding

$$\mathbf{2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O}$$

Excess potassium iodide is added for two reasons:

1. By having the I^- ions in excess, **all** of the $KMnO_4$ reacts completely with the I^- ions to form the maximum amount of I_2, i.e. the equivalent number of moles of I_2.
   - For every two moles of $KMnO_4$ that react, five moles of I_2 are formed.
   - Thus, the amount of iodine formed in the above reaction is directly related to the amount of potassium permanganate.
   - Therefore, if we use a standard solution of $KMnO_4$, we can easily work out the amount of iodine formed.
   - This known amount of iodine formed is then titrated against a sodium thiosulfate solution to calculate the exact concentration of the sodium thiosulfate solution, i.e. to standardise the thiosulfate solution.
2. The presence of the I^- ions helps to keep in solution the iodine that is produced.
   - Iodine (non-polar) is only sparingly soluble in water (a polar solvent) but is readily soluble in potassium iodide solution.
   - When iodine is added to KI solution, the I_2 molecule reacts with the iodide ion to form an ion called the tri-iodide ion, I_3^-.
   - The I_3^- ion, because it is charged, dissolves easily in water.

$$I_2 + I^- \rightarrow I_3^-$$

   - The I_3^- ion is identical in its chemical behaviour to I_2.
   - Therefore, solutions of I_3^- may be treated as solutions of I_2, i.e. a solution of iodine in potassium iodide may be treated as if it were a solution of iodine in water.

How is the end point detected in an iodine/thiosulfate titration?

As already stated, thiosulfate reacts with iodine according to the equation:

$$\underset{\text{reddish brown}}{I_2} + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + \underset{\text{colourless}}{2I^-}$$

As the thiosulfate solution is added to the iodine solution, the reddish-brown colour gradually turns yellow, then paler yellow, then paler still until the solution turns colourless, Figure 15.14.

Since there is no sudden colour change, this would make the end point very difficult to detect. Therefore, it is necessary to use an indicator to detect the end point accurately. The indicator used is starch. Starch indicator forms a blue-black colour with iodine, Figure 15.16. When all of the iodine has reacted with the thiosulfate, the blue-black colour suddenly disappears.

- When performing an iodine/thiosulfate titration, the starch is only added when most of the iodine has disappeared, i.e. when the reddish/ brown colour of the iodine has become pale yellow.
- The reason for this is because if starch were added at an early stage in the titration, the iodine present would become strongly **adsorbed** on to the starch and this would make the titration less accurate, since the iodine would be desorbed slowly to react with the thiosulfate.
- In addition, when the pale yellow colour is observed, it tells us that the end point is near. Then, when the starch is added, the thiosulfate solution can be added drop by drop in order to obtain an accurate titration figure.
- The method of carrying out iodine/thiosulfate titrations is discussed again in the next experiment.

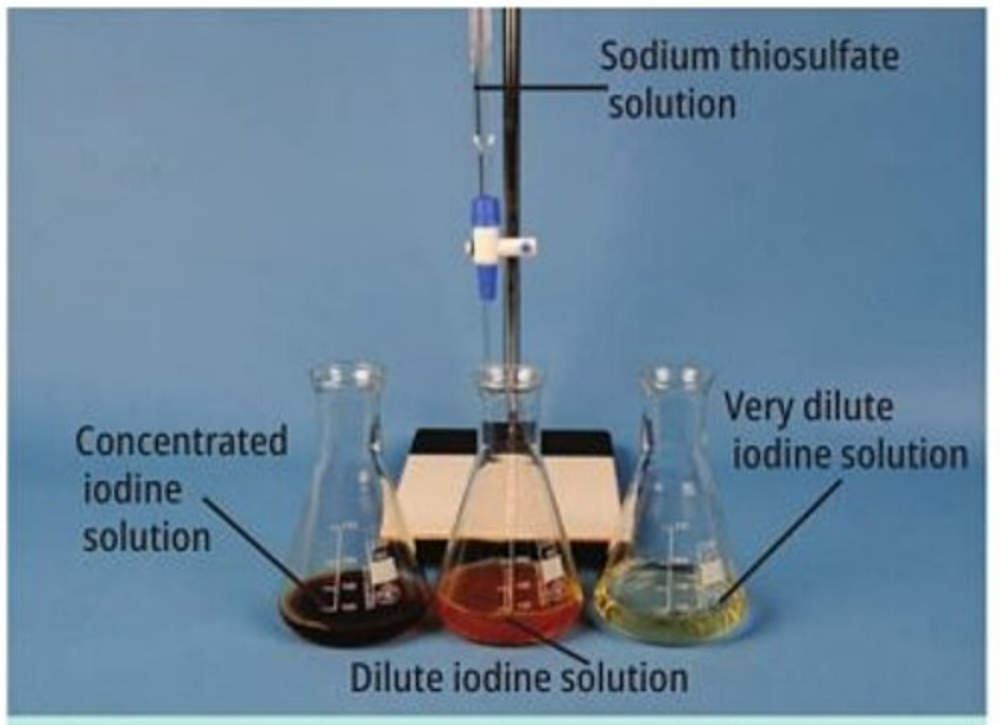


Figure 15.15 As the thiosulfate uses up the iodine, the colour of the solution in the conical flask becomes lighter.

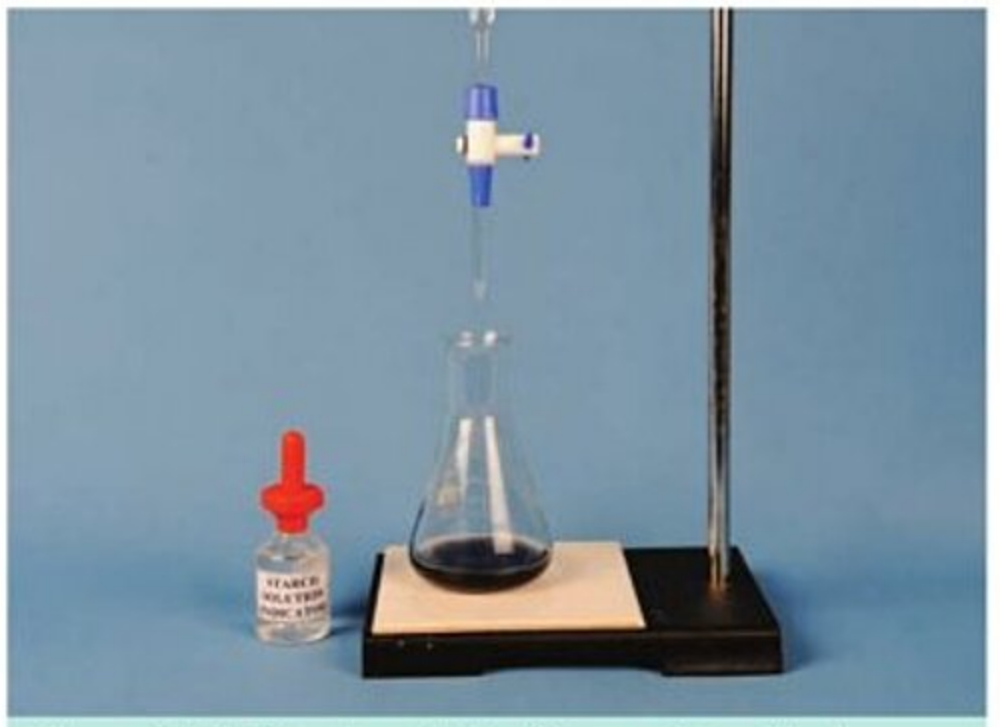


Figure 15.16 Starch solution forms a blue-black complex with iodine.

15.3 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 13 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 13

To prepare a solution of sodium thiosulfate and to standardise it by titration against a solution of iodine

Introduction

In this experiment, we will make up an approximate 0.1 M solution of sodium thiosulfate. We will then find the exact concentration of this solution by titrating it against a solution of iodine. The iodine solution is made by the reaction between acidified $KMnO_4$ solution (of known concentration) and excess iodide ions. The permanganate ions and iodide ions react in the conical flask as follows:

$$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

The iodine formed is then reacted with sodium thiosulfate, which is added from a burette. The following reaction occurs:

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

The experimental set up is illustrated in Figure 15.17.

It is important to use distilled water in this experiment, as tap water contains small quantities of chlorine (an oxidising agent) that may interfere with the result by increasing the amount of iodine present. Remember that chlorine oxidises iodide ions to iodine.

$$Cl_2 + 2I^- \rightarrow 2Cl^- + I_2$$

Deionised water has all of the dissolved ions removed from tap water but could still contain some dissolved chlorine. Using distilled water will ensure a more accurate result but, if distilled water is not available, use deionised water instead.

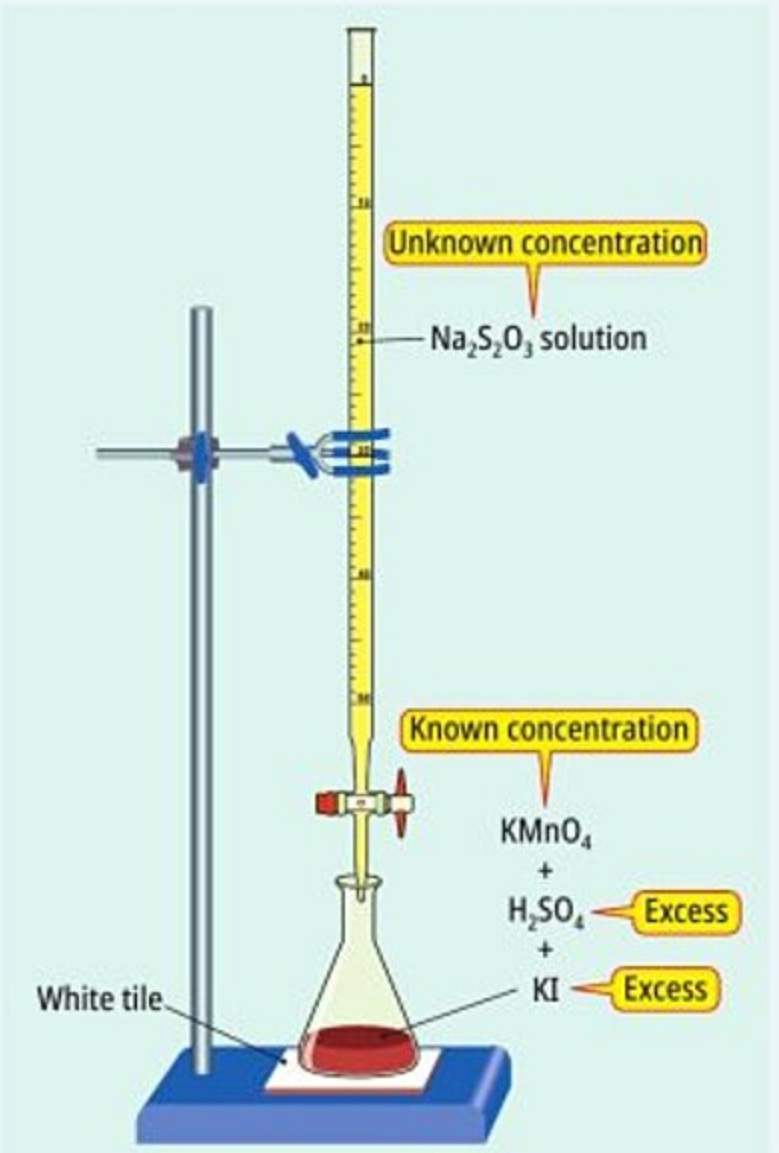


Figure 15.17 Experiment to standardise a solution of sodium thiosulfate

Key steps in procedure

- Some sodium thiosulfate is weighed out on a clock glass using the laboratory balance.
- Taking all the precautions outlined previously, the crystals are transferred to a beaker containing distilled water.
- The solution is stirred to fully dissolve the crystals and, when dissolved, the solution is transferred to a clean volumetric flask with the aid of a funnel.
- All the washings are transferred to the volumetric flask. The bottom of the meniscus of the solution is brought up to the mark with deionised water.
- The stoppered flask is inverted about 20 times.
- The pipette, burette and conical flask are washed with deionised water.
- The burette is washed with some of the sodium thiosulfate solution and filled with the thiosulfate solution using a funnel. The funnel is removed.
- The bottom of the meniscus of the sodium thiosulfate solution is adjusted to the zero mark on the burette.
- A check is made to ensure that the tap and the space below the tap are filled with the sodium thiosulfate solution.

- A standardised $KMnO_4$ solution is poured into a clean, dry beaker. The pipette is washed with a small amount of this solution.
- Using a pipette filler, the pipette is filled to the mark with the $KMnO_4$ solution and this amount of $KMnO_4$ solution is added to the conical flask.
- Using a graduated cylinder, some dilute sulfuric acid is added to the conical flask, making sure that the acid is in excess.

Observation

- The colour of the solution in the conical flask is purple.

Explanation

- The purple colour is the colour of the $KMnO_4$ before it takes part in the reaction.
- The sulfuric acid is added in excess to the potassium permanganate [potassium manganate(VII)] solution in the conical flask in order to supply sufficient H^+ ions for complete reduction of the MnO_4^- ions to Mn^{2+} ions according to the following half equation:

$$MnO_4^- + 8H^+ + 5e^- \rightarrow Mn^{2+} + 4H_2O$$

Procedure (continued)

- Using a graduated cylinder some potassium iodide solution is added in excess to the conical flask.

Observation

- The solution in the conical flask turns a reddish-brown colour.

Explanation

- The reddish-brown colour is due to the iodine that has been formed according to the equation:

$$\underset{\text{purple}}{2MnO_4^- + 10I^- + 16H^+} \rightarrow \underset{\text{reddish-brown}}{2Mn^{2+} + 5I_2} + 8H_2O$$

- The potassium iodide is added in excess for the two reasons stated above: (i) to ensure that **all** of the potassium permanganate has reacted (has been reduced) to produce the corresponding amount of iodine according to the above equation, and (ii) to keep in solution the iodine that is produced.

Procedure (continued)

- A titration is carried out in the usual manner.

Observation

- As the titration proceeds, the dark brown colour of the iodine becomes less intense and gradually changes to a yellow colour and then to a pale yellow colour.

Explanation

- As the sodium thiosulfate solution is added to the conical flask, a reaction takes place between the thiosulfate ions and the iodine according to the following equation:

$$\underset{\text{reddish-brown}}{I_2} + 2S_2O_3^{2-} \rightarrow \underset{\text{colourless}}{S_4O_6^{2-}} + 2I^-$$

As the iodine becomes used up in the above reaction, the reddish-brown colour gradually becomes less intense and fades to a pale yellow colour.

Procedure (continued)

- The titration is continued until the solution in the conical flask becomes pale yellow (straw colour).
- A few drops of starch indicator are added.

Observation

- The solution in the conical flask turns a blue-black colour.

Explanation

- The pale yellow colour tells us that there is very little iodine left in solution, i.e. that the end point is near.
- The blue-black colour is caused by the starch reacting with the small amount of iodine left in solution.

Procedure (continued)

- The titration is continued by adding the thiosulfate solution drop by drop until the blue-black colour disappears.
- The titration figure is noted. One rough and two accurate titrations are carried out. The two accurate titration figures should agree to within 0.1 cm^3.

Explanation

- The fact that the blue-black colour disappears tells us that there is no more iodine left in solution. This means that all of the iodine has reacted with the thiosulfate, i.e. the end point has been reached.
- The colour changes observed in the various stages of this experiment are summarised in Figure 15.18.

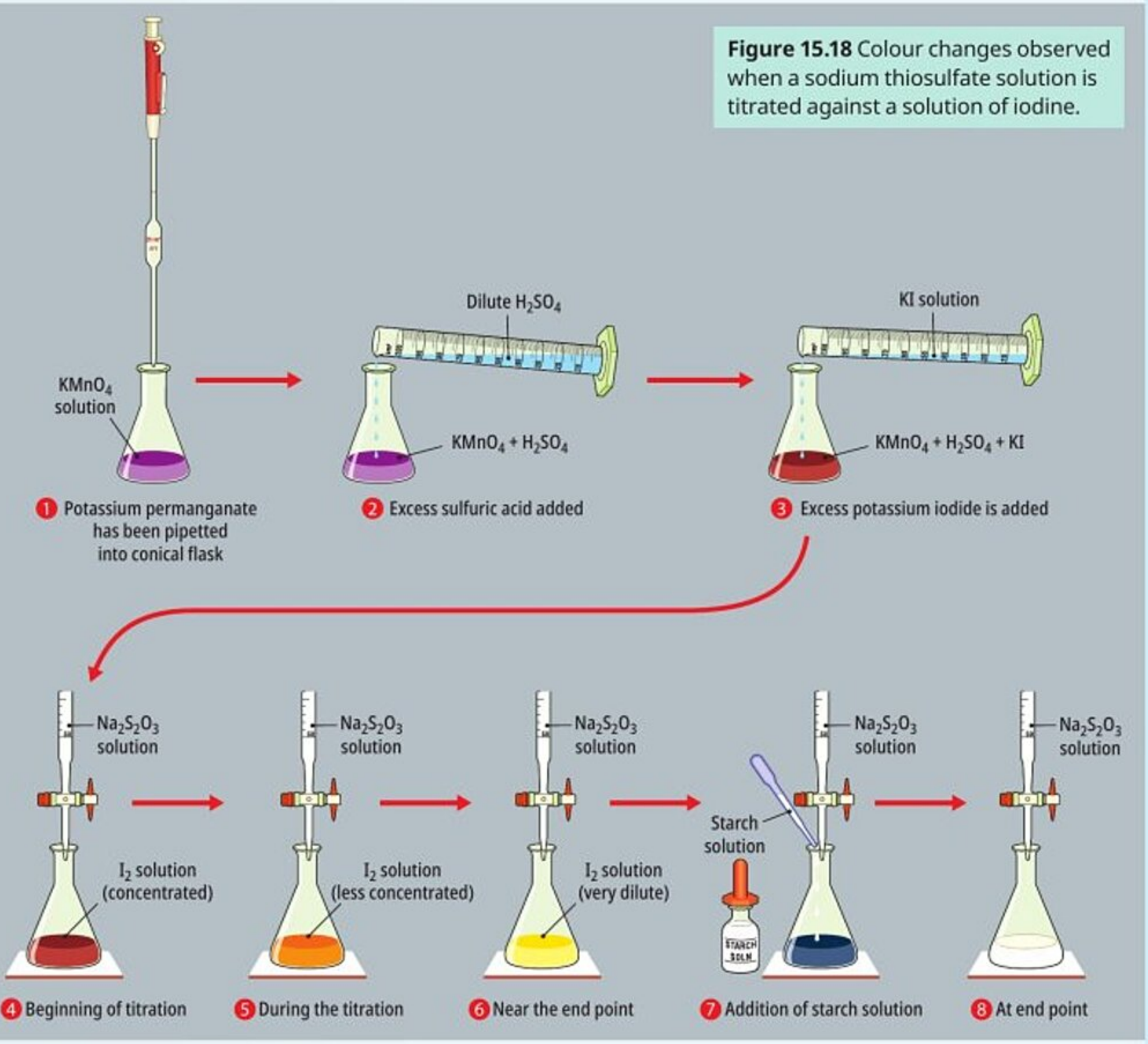


Figure 15.18 Colour changes observed when a sodium thiosulfate solution is titrated against a solution of iodine.

Calculations

The method of calculating the concentration of the sodium thiosulfate solution in iodine/thiosulfate titrations is shown in Examples 15.4 and 15.5.

DIGITAL: A video of this experiment is available on FolensHIVE.

Example 15.4 shows you how to calculate the concentration of a sodium thiosulfate solution when you are given the concentration of the iodine solution. Example 15.5 shows you how to calculate the concentration of a sodium thiosulfate solution when you are given the concentration of the potassium permanganate solution, i.e. the type of calculation involved in Student Experiment No. 13 above.

Example 15.4

Question

25 cm^3 of a 0.045 M iodine solution (previously standardised) were titrated against a solution of sodium thiosulfate. The average titration figure was 27.45 cm^3. Calculate the concentration of the sodium thiosulfate solution in (a) moles per litre and (b) grams per litre of crystalline $Na_2S_2O_3.5H_2O$.

The reaction between iodine and thiosulfate may be represented as:

$$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$$

Answer

Step 1

Calculate the concentration of the sodium thiosulfate solution (reducing agent).

From the balanced equation, we see that two moles of thiosulfate (the reducing agent) react with one mole of iodine (the oxidising agent), i.e. $n_o = 1$ and $n_r = 2$.

I_2 $S_2O_3^{2-}$

Given:

$V_o = 25$

$M_o = 0.045$

$n_o = 1$

$V_r = 27.45$

$M_{red} = ?$

$n_r = 2$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

$$\frac{25 \times 0.045}{1} = \frac{27.45 \times M_{red}}{2}$$

$$M_{red} = \frac{25 \times 0.045 \times 2}{27.45}$$

$$= 0.082 \text{ moles/L}$$

Step 2

Convert to g/L

$= 0.082 \times 248.2$ g/L (Rel. molecular mass of $Na_2S_2O_3.5H_2O = 248.2$)

$= 20.352$ g/L

Answer: Concentration of sodium thiosulfate solution is:

(a) 0.082 moles per litre

(b) 20.352 grams $Na_2S_2O_3.5H_2O$ per litre.

$2 \times Na = 2 \times 22.99$	$= 45.98$
$2 \times S = 2 \times 32.07$	$= 64.14$
$3 \times O = 3 \times 16$	$= 48.00$
$10 \times H = 10 \times 1.008$	$= 10.08$
$5 \times O = 5 \times 16$	$= 80.00$
$M_r\ Na_2S_2O_3.5H_2O$	$= 248.2$

Example 15.5

Question

25 cm^3 of 0.02 M potassium permanganate are pipetted into a conical flask. Some dilute sulfuric acid and excess potassium iodide solution are then added and the liberated iodine is titrated against a solution of sodium thiosulfate of unknown concentration. The average titration figure is 18.7 cm^3. Calculate the concentration of the sodium thiosulfate solution in (a) moles per litre and (b) grams per litre of crystalline $Na_2S_2O_3.5H_2O$.

The reactions may be represented as:

$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

$I_2 + 2S_2O_3^{2-} \rightarrow S_4O_6^{2-} + 2I^-$

Answer

Step 1

Calculate the molarity of the sodium thiosulfate solution (reducing agent)

From the balanced equations, we see that two moles of MnO_4^- produce five moles of I_2 and these five moles of I_2 would then react with ten moles of $Na_2S_2O_3$, i.e. $2MnO_4^- \equiv 5I_2 \equiv 10S_2O_3^{2-}$. This means that $n_o = 2$ and $n_r = 10$.

MnO_4^- $S_2O_3^{2-}$

Given:

$V_o = 25$

$M_o = 0.02$

$n_o = 2$

$V_r = 18.75$

$M_{red} = ?$

$n_r = 10$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

$$\frac{25 \times 0.02}{2} = \frac{18.7 \times M_{red}}{10}$$

$$M_{red} = \frac{25 \times 0.02 \times 10}{2 \times 18.7}$$

$= 0.1337$ moles per litre

Step 2

Convert to g/L

$= 0.1337 \times 248.2$ g/L (Rel. molecular mass of $Na_2S_2O_3.5H_2O = 248.2$)

$= 33.184$ g/L

Answer: Concentration of sodium thiosulfate solution is:

(a) 0.1337 moles per litre

(b) 33.184 grams $Na_2S_2O_3.5H_2O$ per litre.

$2 \times Na = 2 \times 22.99$	$= 45.98$
$2 \times S = 2 \times 32.07$	$= 64.14$
$3 \times O = 3 \times 16$	$= 48.00$
$10 \times H = 10 \times 1.008$	$= 10.08$
$5 \times O = 5 \times 16$	$= 80.00$
$M_r\ Na_2S_2O_3.5H_2O$	$= 248.2$

» Study Example 15.6 in the online resources.

Example 15.7

Question

Acidified solutions of potassium permanganate liberate iodine from iodide solution according to the equation:

$2MnO_4^- + 10I^- + 16H^+ \rightarrow 2Mn^{2+} + 5I_2 + 8H_2O$

When excess potassium iodide was added to 25.0 cm^3 of an acidified solution of potassium permanganate, it required 22.5 cm^3 of 0.125 M sodium thiosulfate solution to reduce the iodine liberated. Calculate the mass of potassium permanganate in the 25.0 cm^3 of solution.

Answer

Step 1

Calculate the concentration of the $KMnO_4$ solution.

$2MnO_4^- \equiv 5I_2 \equiv 10S_2O_3^{2-}$, i.e. $n_o = 2$ and $n_r = 10$.

MnO_4^- $S_2O_3^{2-}$

Given:

$V_o = 25$

$M_o = ?$

$n_o = 2$

$V_r = 22.5$

$M_{red} = 0.125$

$n_r = 10$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

$$\frac{25 \times M_o}{2} = \frac{22.5 \times 0.125}{10}$$

$$M_o = \frac{22.5 \times 0.125 \times 2}{25 \times 10}$$

$= 0.0225$ moles per litre

Step 2

Convert to g/L

$= 0.0225 \times 158.04$ grams per litre (Rel. molecular mass of $KMnO_4 = 158.04$)

$= 3.556$ grams per litre

Step 3

Convert to g/25 cm^3

$$= \frac{3.556}{1000} \times 25$$

$= 0.089$ grams per 25 cm^3

K	= 39.1
Mn	= 54.94
$4 \times O = 4 \times 16$	= 64.00
$M_r\ KMnO_4$	= 158.04

Answer: Mass of $KMnO_4$ in 25 cm^3 of solution = 0.089 grams.

TEST YOURSELF: Attempt Questions 15.10–15.11 and W15.9–W15.11.

Summary What I should know

- Potassium permanganate [potassium manganate(VII)] is an oxidising agent.
- Potassium permanganate is not a primary standard.
- Potassium permanganate acts as its own indicator when it is used in titrations.
- Potassium permanganate oxidises Fe^{2+} ions to Fe^{3+} ions in acidified solution.
- One of the equations used for analysing data from titrations involving redox reactions is:
$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$
- Sodium thiosulfate is a reducing agent. It reduces iodine molecules to iodide ions.
- A solution of sodium thiosulfate is standardised by titration against a solution of iodine.
- Starch is used to detect the end point in an iodine/thiosulfate titration.

Learning outcomes

At the end of this chapter, I should be able to:			
Outline some properties of potassium permanganate [potassium manganate(VII)].	⬡	⬡	⬡
Discuss the reaction between MnO_4^- ions and Fe^{2+} ions.	⬡	⬡	⬡
Standardise a solution of potassium permanganate in the laboratory using a standard solution of ammonium iron(II) sulfate.	⬡	⬡	⬡
Use volumetric analysis to determine the amount of iron in an iron table.	⬡	⬡	⬡
Discuss the properties of sodium thiosulfate.	⬡	⬡	⬡
Prepare a solution of sodium thiosulfate in the laboratory and standardise it by titration against a solution of iodine.	⬡	⬡	⬡

Chapter review questions

Use the following values of relative atomic masses in answering these questions:
H = 1.008, C = 12.01, N = 14.01, O = 16, Na = 22.99, S = 32.07, Cl = 35.45, K = 39.10, Mn = 54.94, Fe = 55.85, I = 126.9.

15.1 The potassium permanganate product shown in Figure 15.19 is advertised as effective to prevent external fish infections from fungi, bacteria and parasites. It can also be used to remove Fe^{2+} ions from water.

Figure 15.19

(a) Write the formula for potassium permanganate.

(b) What is the more modern (systematic) name for potassium permanganate?

(c) What is the oxidation number of Mn in potassium permanganate?

(d) Write a balanced chemical equation for the reaction between permanganate ions and Fe^{2+} ions in acidic solution.

(e) Identify the oxidising agent and reducing agent in the equation that you have written in (iv).

15.2 A student made up a 0.15 M ammonium iron(II) sulfate solution and used this to standardise a solution of potassium permanganate [potassium manganate(VII)]. 25 cm^3 of the ammonium iron(II) sulfate solution were titrated against the potassium permanganate solution. The average titration figure was 22.85 cm^3. Calculate the concentration of the potassium permanganate solution in (a) moles per litre and (b) grams per litre.

15.3 It was found that 25 cm^3 of a solution of iron(II) sulfate reacted with 23.45 cm^3 of 0.02 M $KMnO_4$ solution. Calculate the concentration of the iron(II) sulfate solution in (a) moles per litre and (b) grams of crystalline $FeSO_4.7H_2O$ per litre. What other substance, apart from the iron(II) sulfate solution, should be added to the conical flask? Give the reason for adding this other substance.

15.4 A student weighed out 10.52 g of ammonium iron(II) sulfate crystals, $(NH_4)_2SO_4.FeSO_4.6H_2O$, dissolved them in dilute sulfuric acid and made the solution up to 250 cm^3 in a volumetric flask. 25 cm^3 of this solution reacted with 23.8 cm^3 of a solution of potassium permanganate. Calculate the concentration of the potassium permanganate solution in (a) moles per litre and (b) grams of crystalline $KMnO_4$ per litre.

15.5 A mass of 6.08 grams of iron(II) sulfate crystals ($FeSO_4.xH_2O$) was dissolved in deionised water which had been acidified with dilute sulfuric acid. The resulting solution was made up to 250 cm^3 in a volumetric flask. 25 cm^3 of this solution required 21.8 cm^3 of 0.02 M $KMnO_4$ solution for complete reaction.

(a) Outline the procedure for transferring the crystals to the volumetric flask.

(b) Why was it necessary to acidify the deionised water used to dissolve the crystals?

(c) In carrying out the titration, it was also necessary to add sulfuric acid to the conical flask. What is the reason for this? What would be observed if sulfuric acid were not added to the conical flask?

(d) Calculate the value of x in the above formula.

15.6 A mass of 9.80 g of ammonium iron(II) sulfate crystals, $(NH_4)_2SO_4.FeSO_4.xH_2O$, was dissolved in dilute sulfuric acid and the resulting solution was made up to 250 cm^3 in a volumetric flask. 25 cm^3 of this solution were titrated against 0.021 M $KMnO_4$ solution. The average titration figure was 23.85 cm^3. Calculate the value of x in the above formula.

15.7 A chemist dissolved 7.84 g of ammonium iron(II) sulfate, $(NH_4)_2SO_4.FeSO_4.xH_2O$, in dilute sulfuric acid and made up the solution to 250 cm^3 with distilled water. 25 cm^3 of this solution required 20 cm^3 of 0.02 M potassium manganate(VII) (potassium permanganate) for complete reaction according to the equation:

$$5Fe^{2+} + MnO_4^- + 8H^+ \rightarrow 5Fe^{3+} + Mn^{2+} + 4H_2O$$

Chapter review questions

(a) Why was dilute sulfuric acid used in making up the iron(II) salt solution?

(b) Find the concentration, in moles per litre, of Fe^{2+} ions in the solution.

(c) Find the value of x.

(d) Show clearly any changes in oxidation numbers which have occurred in the reaction. [LCH]

15.8 Five tablets of total mass 1.69 g and containing iron(II) sulfate were dissolved in dilute sulfuric acid and made up to 250 cm^3 in a volumetric flask. 20 cm^3 portions of the resulting solution were titrated against 0.01 M potassium permanganate [potassium manganate(VII)]. The average titration figure was 9.15 cm^3.

(a) Name the piece of apparatus used to measure (a) 25 cm^3 of the iron(II) sulfate solution and (b) to measure approximately 20 cm^3 of dilute sulfuric acid.

(b) Describe how the end point is detected in this titration.

(c) Calculate (i) the mass of anhydrous $FeSO_4$ in each tablet, (ii) the mass of iron in each tablet and (iii) the percentage of $FeSO_4$ in each tablet. The equation for the reaction is:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

15.9 In an analysis of iron tablets to determine the amount of iron sulfate per tablet, four tablets whose total mass was 0.96 g were dissolved in dilute sulfuric acid and made up to 250 cm^3 in a volumetric flask. 25 cm^3 portions of the resulting solution were titrated against 0.015 M potassium permanganate. The average titration figure was 4.51 cm^3.

(a) Why are the tablets dissolved in dilute sulfuric acid?

(b) Why is dilute sulfuric acid added to the tablet solution in the conical flask before titrating?

(c) What is observed as the potassium permanganate solution is added to the iron(II) sulfate solution?

(d) Calculate (i) the mass of anhydrous $FeSO_4$ in each tablet, (ii) the mass of iron in each tablet and the percentage of $FeSO_4$ in each tablet. The equation for the reaction is:

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

15.10 Sodium thiosulfate is used as an antidote for cyanide poisoning, Figure 15.20. It reacts with cyanide ions as follows:

$$Na_2S_2O_3 + CN^- \rightarrow SCN^- + Na_2SO_3$$

Figure 15.20

(a) Describe the appearance of sodium thiosulfate.

(b) Indicate the oxidising and reducing agents in the above reaction.

(c) Draw the Lewis structure of the $S_2O_3^{2-}$ ion.

(d) Some sodium thiosulfate was added to water containing chlorine and the following reaction took place:

$$Na_2S_2O_3 + Cl_2 + H_2O \rightarrow 2NaHSO_4 + HCl$$

Assign oxidation numbers and balance the above equation.

(e) Give an everyday application of the above reaction.

15.11 25 cm^3 of a 0.05 M iodine solution (previously standardised) were titrated against a solution of sodium thiosulfate. The average titration figure was 18.55 cm^3. Calculate the concentration of the sodium thiosulfate solution in (a) moles per litre and (b) grams per litre of crystalline $Na_2S_2O_3.5H_2O$. The reaction between iodine and thiosulfate may be represented as:

$$2S_2O_3^{2-} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$$

16 Oxidation–Reduction Volumetric Exam-Style Questions

OBJECTIVES

- To introduce students to a range of different types of questions in volumetric analysis involving oxidation–reduction reactions.
- To give students practice in solving oxidation–reduction volumetric problems from first principles and also by using some key formulas.
- To ensure that students can identify and discuss potential sources of errors in practical work involving volumetric analysis.

16.1 Introduction

In Chapter 13, we learned that many problems in acid–base volumetric analysis can be solved from first principles. Having now studied the concepts of oxidation–reduction reactions in Chapters 14 and 15, we will now see how we can apply this knowledge to solve problems in volumetric analysis involving oxidation–reduction reactions. As was done in Chapter 13, we will begin by studying some key formulas to help us solve these volumetric problems and we will also make use of first principles methods that do not require the use of any formulas. When solving a problem in an exam paper from first principles or by using formulas, always remember that it is very important to show all your work.

16.2 Key formulas for solving volumetric problems

The same key formulas as used in Chapter 13 will be used in this chapter. These key formulas are summarised in Table 16.1. We will then show how these key formulas can be used in solving some volumetric problems in exam-style questions.

	Formula	Comment
1.	Number of moles = $\frac{\text{Mass (in grams)}}{\text{Relative Molecular Mass}}$	This is a very useful formula (Chapter 8) for calculating the number of moles of a substance when we know the relative molecular mass. It can also be manipulated to (i) calculate the mass if we know the number of moles and relative molecular mass or (ii) calculate the relative molecular mass if we know the mass and number of moles.
2.	Number of moles = $\frac{\text{volume}^* \times \text{molarity}}{1000}$ (*in cm^3)	This is a very useful formula for calculating the number of moles when given a volume of solution and the molarity of the solution.
3.	$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$	This is a very useful formula for calculating the unknown concentration of a solution from titration data.
4.	Density = $\frac{\text{Mass}}{\text{Volume}}$	This formula is very useful if we are given the density of a liquid and its volume and we need to calculate the mass of the liquid.

Table 16.1 Some key formulas in volumetric analysis

16.3 Solving exam-style problems

We will now study some examples of exam-style questions to show you how the above formulas can be used. The relative atomic masses of the most commonly encountered elements in oxidation–reduction volumetric analysis are given in Table 16.2.

Table 16.2 Relative atomic masses of elements commonly encountered in oxidation–reduction volumetric problems.

Element	Relative atomic mass	Element	Relative atomic mass
H	1.008	S	32.07
C	12.01	Cl	35.45
N	14.01	K	39.1
O	16.00	Mn	54.94
Na	22.99	Fe	55.85
Mg	24.31	I	126.9

Example 16.1

Question

(a) The reagent $(NH_4)_2SO_4.FeSO_4.6H_2O$ (hydrated ammonium iron(II) sulfate) was used to prepare a standard solution. State two properties of this substance that make it suitable for use as a primary standard. [LCH]

EXAM TIP!

Note that this question essentially asks for a definition of a primary standard. So make sure you know this definition!

Answer

Hydrated ammonium iron(II) sulfate can be used as a primary standard because it can be obtained in a **stable**, **pure** and **soluble solid** form so that it can be weighed out and dissolved in water to a solution of accurately known concentration. In addition, it **does not absorb water** (**not hygroscopic**) or **does not lose water of crystallisation** (**not efflorescent**).

Question

(b) (i) Describe how you would prepare exactly 250 cm^3 of a standard solution containing 9.31 g of $(NH_4)_2SO_4.FeSO_4.6H_2O$ (hydrated ammonium iron(II) sulfate) that was supplied on a clock glass.

Answer

The detailed steps should be studied carefully in Experiment 11 of the Laboratory Notebook accompanying this textbook. The following is a summary of the main steps:

1. Dissolve the crystals in a beaker containing deionised water and dilute sulfuric acid.
2. Add the washings of the clock glass to the beaker.
3. Transfer the contents of the beaker to the 250 cm^3 volumetric flask.
4. Use a funnel when transferring the contents of the beaker to the 250 cm^3 volumetric flask.
5. Add the washings of the beaker, funnel and glass rod to the 250 cm^3 volumetric flask.
6. Add deionised water to the volumetric flask until the water is near the graduation mark.
7. When the meniscus of the water is near the graduation mark of the volumetric flask, carefully use a dropper to add water.
8. Ensure that the bottom of the meniscus is on the graduation mark.
9. Stopper the volumetric flask.
10. Invert the stoppered flask about 20 times.

Question

(ii) Why was dilute sulfuric acid added during the preparation of this standard solution?

Answer

The sulfuric acid prevents the Fe^{2+} ions being oxidised to Fe^{3+} ions by the oxygen in the air.

Question

(c) This standard solution of Fe^{2+} ions was used to determine by titration the concentration of a potassium manganate(VII) solution. The balanced equation for the titration reaction is:

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

In each titration, a little dilute sulfuric acid was added to a 25.0 cm^3 portion of the Fe^{2+} ion solution in a conical flask before adding the potassium manganate(VII) solution from a burette. On average, 22.6 cm^3 of the $KMnO_4$ solution were required for complete reaction with 25.0 cm^3 of the solution of the Fe^{2+} ions in excess acid.

(i) How was the end point of each titration detected?

Answer: A faint permanent pink colour is observed at the end point.

Question

(ii) If insufficient acid was present in the conical flask, what would have been observed as the $KMnO_4$ solution was added from the burette to the Fe^{2+} ion solution? Explain.

Answer: If insufficient acid was present in the conical flask, a brown solid precipitate would be observed.

This brown solid precipitate is due to the formation of manganese dioxide, MnO_2.

(d) (i) Calculate the concentration of $(NH_4)_2SO_4.FeSO_4.6H_2O$ in the standard solution in moles per litre.

Answer

Relative molecular mass of $(NH_4)_2SO_4.FeSO_4.6H_2O$ = 392.17

Working from first principles: 392.17 g in 1 L solution → 1M solution

$$1 \text{ g in 1 L solution} \rightarrow \frac{1}{392.17} \text{ M solution}$$

$$9.31 \text{ g in 1 L solution} \rightarrow \frac{9.31}{392.17} \text{ M solution}$$

$$9.31 \text{ g in 250 cm}^3 \text{ solution} = \frac{9.31 \times 4}{392.17}$$

$$= 0.095 \text{ M solution}$$

The concentration of $(NH_4)_2SO_4.FeSO_4.6H_2O$ = 0.095 M

Calculate M_r of $(NH_4)_2SO_4.FeSO_4.6H_2O$

$2 \times N = 2 \times 14.01$	$= 28.02$
$20 \times H = 20 \times 1.008$	$= 20.16$
$2 \times S = 2 \times 32.07$	$= 64.14$
$14 \times O = 14 \times 16$	$= 224$
$1 \times Fe = 1 \times 55.85$	$= 55.85$
	$M_r = 392.17$

Alternatively, using Formula 1:

$$\text{Number of moles} = \frac{\text{Mass}}{\text{Relative Molecular Mass}} = \frac{9.31}{392.17} = 0.02374 \text{ moles in 250 cm}^3 \text{ volumetric flask}$$

Therefore, concentration in moles/L = $0.02374 \times 4 = 0.095$ M solution

Question

(ii) Calculate the number of moles of Fe^{2+} ion in a 25.0 cm^3 portion of the standard solution.

Answer: Using Formula 2: No. of moles $Fe^{2+} = \frac{\text{volume} \times \text{molarity}}{1000} = \frac{25 \times 0.095}{1000} = 0.002375$ moles

Question

(iii) Calculate the number of moles of potassium manganate(VII) reduced to Mn^{2+} by this quantity of Fe^{2+} ion.

Answer: From the balanced equation, one mole of MnO_4^- ions reacts with 5 moles of Fe^{2+} ions

$$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

Therefore, number of moles of MnO_4^- ions $= \frac{0.002375}{5} = 0.000475$ moles

Question

(iv) Calculate the concentration of the potassium manganate(VII) solution in moles per litre.

Answer

Step 1

Use Formula 3.

MnO_4^- Fe^{2+}

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

Given:

$V_o = 22.6$

$M_o = ?$

$n_o = 1$

$V_r = 25$

$M_{red} = 0.095$

$n_r = 5$

Step 2

Substitute in the values $\frac{22.6 \times M_o}{1} = \frac{25 \times 0.095}{5}$

Step 3

Solve for the unknown (molarity of $KMnO_4$):

$$M_o = \frac{25 \times 0.095}{5 \times 22.6} = 0.021 \text{ mole/L}$$

The concentration of the potassium manganate(VII) solution is 0.021 M.

Example 16.2

Question

Sodium thiosulfate is a reducing agent that reacts with iodine according to the following balanced equation:

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

To determine the concentration of a sodium thiosulfate solution, a student titrated it against 25.0 cm^3 portions of a standard iodine solution. [LCH]

(a) Explain how iodine, a non-polar substance of very low water solubility, is brought into aqueous solution.

Answer

Iodine is brought into aqueous solution since, when added to KI solution, the I_2 molecule reacts with the iodide ion. In this reaction, an ion called the tri-iodide ion (I_3^-) is formed. Since the I_3^- ion is charged, it dissolves easily in water.

$$I_2 + I^- \rightarrow I_3^-$$

Question

(b) The iodine solution was made up in a 500 cm^3 volumetric flask. Describe the procedure for measuring 25.0 cm^3 of this solution into a conical flask.

Answer

The main steps for measuring 25 cm^3 of an iodine solution into a conical flask are:

1. Pour the iodine solution into a **clean**, **dry beaker**.
2. Obtain a 25 cm3 pipette.
3. Rinse out the pipette with deionised water.
4. Also rinse out the pipette with the iodine solution.
5. Using a pipette filler, bring the bottom of the meniscus of the iodine solution to the graduation mark in the pipette.
6. Read the meniscus at eye level.
7. Allow the iodine solution in the pipette to drain into the conical flask.
8. When the discharge is complete, touch the tip of the pipette against the side of the conical flask.
9. Wait a few seconds before removing the pipette (draining time).
10. Allow the last drop in the pipette to remain there – do not blow it into the conical flask.

Question

(c) Name a suitable indicator for this titration.

At what stage is the indicator added?

State the colour change at the end point in the presence of the indicator.

Answer

- A suitable indicator is starch.
- The indicator is added when the solution in the conical flask is a pale yellow (straw) colour. The pale yellow (straw) colour tells you that nearly all the iodine is used up, i.e. the end point is near.
- The colour change at the end point is blue-black to colourless.

EXAM TIP!

When you are asked for a colour change, you must always state the initial colour and the final colour, i.e. two colours! Also note that 'clear' is not accepted for 'colourless' as a clear solution can be coloured.

Question

(d) Given that there were 6.35 g of iodine (I_2) in 500 cm^3 of the iodine solution,

(i) Calculate the number of moles of iodine in each 25.0 cm^3 portion.

Answer

Use Equation 1:

$$\text{Number of moles } I_2 = \frac{\text{Mass (in grams)}}{\text{Relative Molecular Mass}} = \frac{6.35}{253.8} = 0.025 \text{ moles}$$

500 cm^3 of iodine solution contains 0.025 mole I_2

1 cm^3 of iodine solution contains $\frac{0.025}{500}$ mole I_2

25 cm^3 of iodine solution contains $\frac{0.025 \times 25}{500} = 0.00125$ mole I_2

Question

(ii) Calculate the number of moles of sodium thiosulfate required to reduce this quantity of iodine.

Answer

From the balanced equation $I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$

Two moles of thiosulfate react with every mole of iodine.

Therefore, $2 \times 0.00125 = 0.0025$ moles of sodium thiosulfate are required to react with 0.00125 mole I_2.

Question

(iii) Calculate the concentration of the sodium thiosulfate solution in moles per litre, 17.85 cm^3 of which were required to reduce 25.0 cm^3 of the iodine solution,

Answer

Calculate the concentration of the iodine solution:

From (i) above 500 cm^3 of iodine solution contains 0.025 mole I_2

Therefore, 1000 cm^3 of iodine solution contains $0.025 \times 2 = 0.05$ mole I_2

Concentration of I_2 solution = 0.05M

Step 1

Use Formula 3.

I_2 $S_2O_3^-$

$$\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$$

Given:

$V_o = 25.0$

$M_o = 0.05$

$n_o = 1$

$V_r = 17.85$

$M_{red} = ?$

$n_r = 2$

Step 2

Substitute in the values $\frac{25 \times 0.05}{1} = \frac{17.85 \times M_{red}}{2}$

Step 3

Solve for the unknown (molarity of $Na_2S_2O_3$):

$$M_{red} = \frac{25 \times 0.05 \times 2}{17.85} = 0.140 \text{ mole/L}$$

The concentration of the sodium thiosulfate solution is 0.14 M.

$2 \times Na = 2 \times 22.99$	$= 45.98$
$2 \times S = 2 \times 32.07$	$= 64.14$
$3 \times O = 3 \times 16$	$= 48.00$
$10 \times H = 10 \times 1.008$	$= 10.08$
$5 \times O = 5 \times 16$	$= 80.00$
Mr $Na_2S_2O_3.5H_2O$	$= 248.2$

Question

(iv) Calculate the concentration of the sodium thiosulfate solution in grams per litre of its crystals ($Na_2S_2O_3.5H_2O$).

Answer

A 1 M solution of $Na_2S_2O_3.5H_2O$ contains 248.2 g/L

Therefore, a 0.14 M solution of $Na_2S_2O_3.5H_2O$ contains $248.2 \times 0.14 = 34.748$ g/L

Question

(e) Explain why the use of *distilled* water instead of *deionised* water throughout this experiment would be likely to ensure a more accurate result.

Tap water contains small quantities of chlorine (an oxidising agent) that may interfere with the result by increasing the amount of iodine present. Deionised water has all of the dissolved ions removed from tap water, but deionised water could still contain some dissolved chlorine.

TEST YOURSELF: Attempt Questions 16.1–16.5 and W16.1–W16.5.

16.4 Random and systematic errors in chemistry practical work

When carrying out laboratory practical work, there is always a possibility of experimental error.

Experimental error refers to the difference between the measured value and the true value of a particular quantity.

For example, when carrying out laboratory practical work in the area of volumetric analysis, it is important to measure volumes of liquids accurately and precisely. Therefore, we must be aware of sources of error and how to minimise them.

There are two main categories of experimental error: systematic error and random error. We now discuss each of these.

1. Systematic error

A **systematic error** is a consistent, repeating error that always occurs in one direction, i.e. it is always higher or always lower than the true value.

The word 'systematic' means 'something that follows a pattern' or 'a fixed, planned way of carrying out a task'. Having a systematic plan for exam revision is good. However, systematic errors in carrying out laboratory work are bad! An example of a systematic error is where a laboratory balance **always** gives an incorrect reading (too high or too low) in the same direction when in use. If the balance has not been correctly calibrated, every reading could be, say, 1 gram more than it should be.

Other examples of systematic errors due to instrumentation are:

- A faulty pH probe that always provides a reading of a pH value that consistently gives a higher reading than the true value.
- A pipette whose tip has been damaged and always delivers a consistently lower volume of liquid than stated on the bulb of the pipette.

Examples of systematic errors caused by a person who does not follow the correct procedure:

- If the volume of liquid delivered from a burette is always read in an incorrect fashion, a systematic error arises, Figure 16.1. **Parallax error** is the name used to describe the situation of an observer reading the meniscus from an incorrect angle. This means that the measured volume will always be different from the true volume by the same amount.

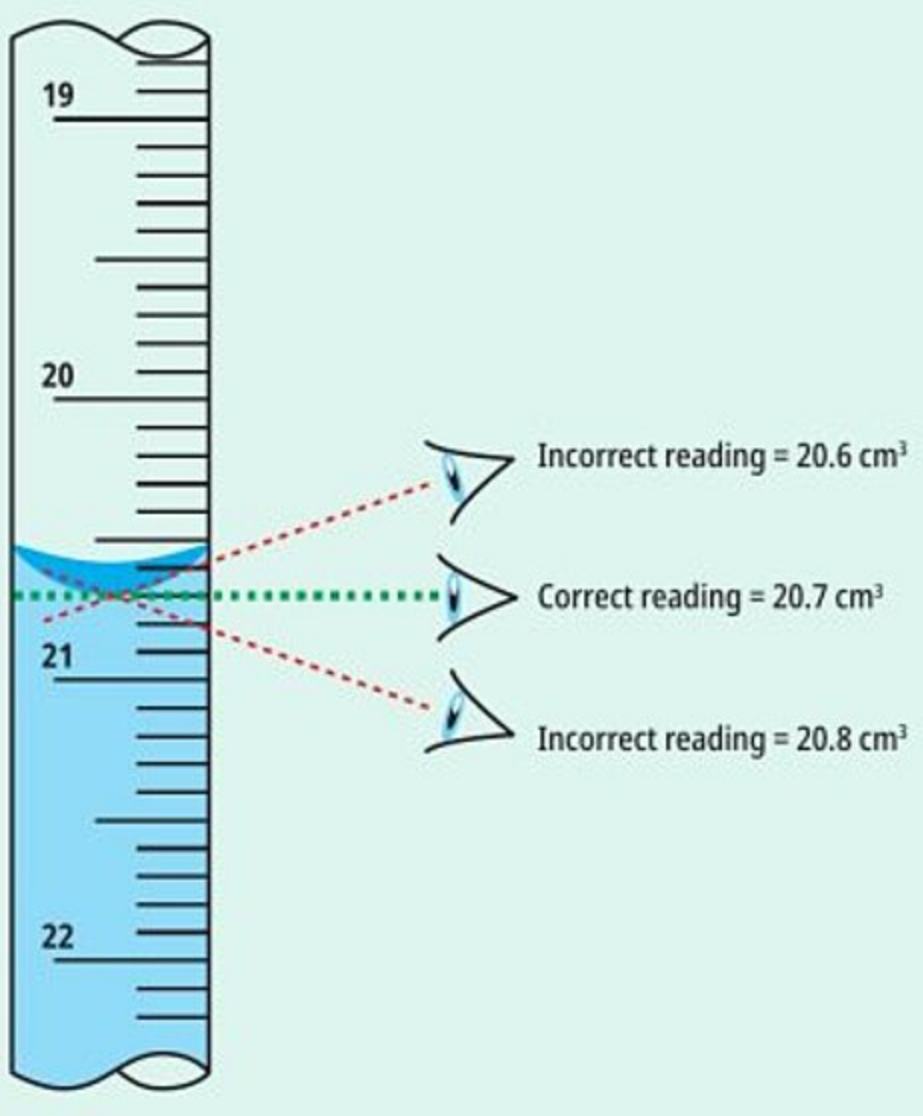


Figure 16.1 A systematic error arises if the volume of liquid in a burette is always read from the top (or always read from the bottom) instead of at eye-level.

The main points about systematic errors may be summarised as follows:

- Systematic errors are consistent, repeating errors that always lead to a deviation from the true value.
- Systematic errors shift all measurements consistently in one direction. In other words, systematic errors cause all measurements to be consistently too high or too low compared to the true value. In short, a characteristic of systematic errors is that they have a consistent bias in one direction.
- Systematic errors cannot be reduced or eliminated by repeated trials – they can only be corrected by undertaking measures such as fixing calibration of instruments or correcting wrong techniques.
- Systematic errors reduce accuracy, as all values are shifted in one direction.
- Systematic errors do not usually affect precision, as all the incorrect results could still be clustered close together.

Systematic errors can be minimised when we:

- Ensure instruments are calibrated correctly before use.
- Use the correct indicators at all times.
- Read volumes of liquids in instruments such as burettes and pipettes at eye-level.
- Follow the correct procedure as outlined in laboratory manuals.

2. Random error

A **random error** is an unpredictable fluctuation in a measurement around the true value that occurs due to variations in experimental conditions and procedures.

The word 'random' means that something is 'unpredictable or unplanned' or that it 'changes without any fixed pattern'. Unlike systematic errors, which happen the same way every time, random events have no pattern and can happen in different ways each time.

Examples of random errors are:

- Air currents affecting the reading of an electronic balance can give rise to random errors each time the balance is used during the experiment.
- Uneven mixing of solutions in a volumetric flask or conical flask can also give rise to random errors. For example, when performing a titration, the conical flask must be continuously shaken in a similar manner during each trial of the titration. If the conical flask is shaken continuously during one trial and shaken very little during a second trial, this could give rise to a random error in trying to detect the end point.
- Similarly, when making up a solution in a volumetric flask, the flask needs to be inverted the same number of times to ensure thorough mixing. Otherwise, variations in the end point could be obtained since the concentration of the solution may not be uniform throughout the solution.
- Failure to wash down the sides of the flask with deionised water at regular intervals during each trial of the titration could also give rise to random errors.
- Human reaction time could cause variations in starting and stopping stopwatches when measuring times for reactions to take place. (This will be discussed in more detail in Chapter 17.)
- Fluctuations in room temperature that could affect the rate of the reaction could also cause random errors. (This will also be discussed in more detail in Chapter 17.)

- A random error could also occur if there is variation in the number of drops of indicator added during each trial of the titration. When we study the theory of how indicators work (Chapter 19), we will see that it is important to ensure that there is consistency in the number of drops of indicator added in each trial of the titration. The recommended number of drops in the laboratory manual should always be used consistently in each trial of the titration.
- A random error could also occur if there is a change in lighting conditions in the lab during the experiment. These changes could affect the difficulty or ease of determining the colour change, as intensity of colours can vary in the presence of bright sunlight or in a less bright environment. Figure 16.4.

Figure 16.4 Lack of consistency in adding the same number of drops of indicator during each trial of the titration can give rise to random errors.

NOTE

1. Incorrectly reading the volume of liquid in a burette or pipette could also be categorised as a random error. For example, if there is no consistency in reading the volume, i.e. in trial 1 of the titration the reading is taken at eye level with the meniscus, in trial 2 the reading is taken from above, and in trial 3 the reading is taken from below.
2. Misjudging the end point could also be categorised as a random error. For example, in one trial the titration could be stopped early and in the next trial the end point could be overshot. This leads to fluctuations around the true value.

The main points about random errors may be summarised as follows:

- Unlike systematic errors, which always shift the results in one direction, random errors cause measurements to fluctuate in both directions around the true value.
- Random errors are unpredictable and inconsistent.
- Random errors can be reduced by repeating measurements and averaging results. For example, you could overshoot the end point due to a random error in interpreting the colour change. This may be caused by a change in the lighting conditions of the room. The random error can be corrected by repeating the titration and averaging two values that agree to within 0.1 cm^3.
- Random errors may not necessarily affect accuracy due to repeated measurements being taken and averaging of results.
- Random errors affect precision because random errors give rise to results that are scattered from each other rather than being clustered close together.
- Random errors can be minimised by keeping the room conditions the same (controlled conditions) throughout the experiment.

It is important in volumetric analysis that results are accurate and precise. By recognising systematic and random errors, we can take steps to minimise them.

Example 16.3

Question

A student prepares a solution using a volumetric flask but fails to ensure that the solution in the volumetric flask is mixed thoroughly by forgetting to invert the flask several times before using the solution in a titration.

Question

(a) Explain the type of error introduced into the experiment.

Answer

This introduces a random error because different samples could have different concentrations due to the incomplete mixing.

Question

(b) Explain how this error will affect the titration results.

Answer

Since different samples could have different concentrations in each trial of the titration, the titration figure in some trials may be high and in other trials may be low.

- A systematic error also arises if the wrong indicator is used for a particular titration. The correct indicator specified in the laboratory manual for each particular type of titration must always be used. Using the wrong indicator for each titration in a set of titrations to measure an unknown concentration will give rise to errors in detecting the end point. If the wrong indicator is used in a titration, the end point may be detected too early or too late. The reason for this is because different indicators change colour at different pH values. (We will explain this in more detail in Chapter 19.)
- A systematic error arises if the correct procedure for rinsing out glassware is not followed. The rinsings required are summarised in Figure 16.2.
  - If a burette is only rinsed with deionised water, the water remaining in the burette will dilute the solution added to the burette. This 'more dilute' solution will introduce an error to the volume added at the end point since a greater volume of the diluted solution will be required for complete reaction.
  - If a pipette is only rinsed with deionised water, the water remaining in the pipette will dilute the solution drawn into the pipette. This error will mean that a lower amount of solution will need to be added from the burette to completely react with the 'more diluted' solution from the pipette.
  - If the conical flask is rinsed with the solution it is to contain, this means that an additional volume of solution (i.e. in addition to the solution that is added from the pipette) has been added to the conical flask. This error will result in a greater volume of solution having to be added to the conical flask from the burette to fully react with the solution in the conical flask.

These errors in rinsings are classified as systematic errors, as they always affect the results in a specific direction.

- Another example of a systematic error would be if the end point is always overshot. For example, suppose a student does not realise, when using $KMnO_4$, that the end point is when a faint permanent pink colour is observed. Instead, the student always takes the end point when a strong purple colour is formed, Figure 16.3. Therefore, all of the titre readings will be too high, i.e. shifted in one direction.

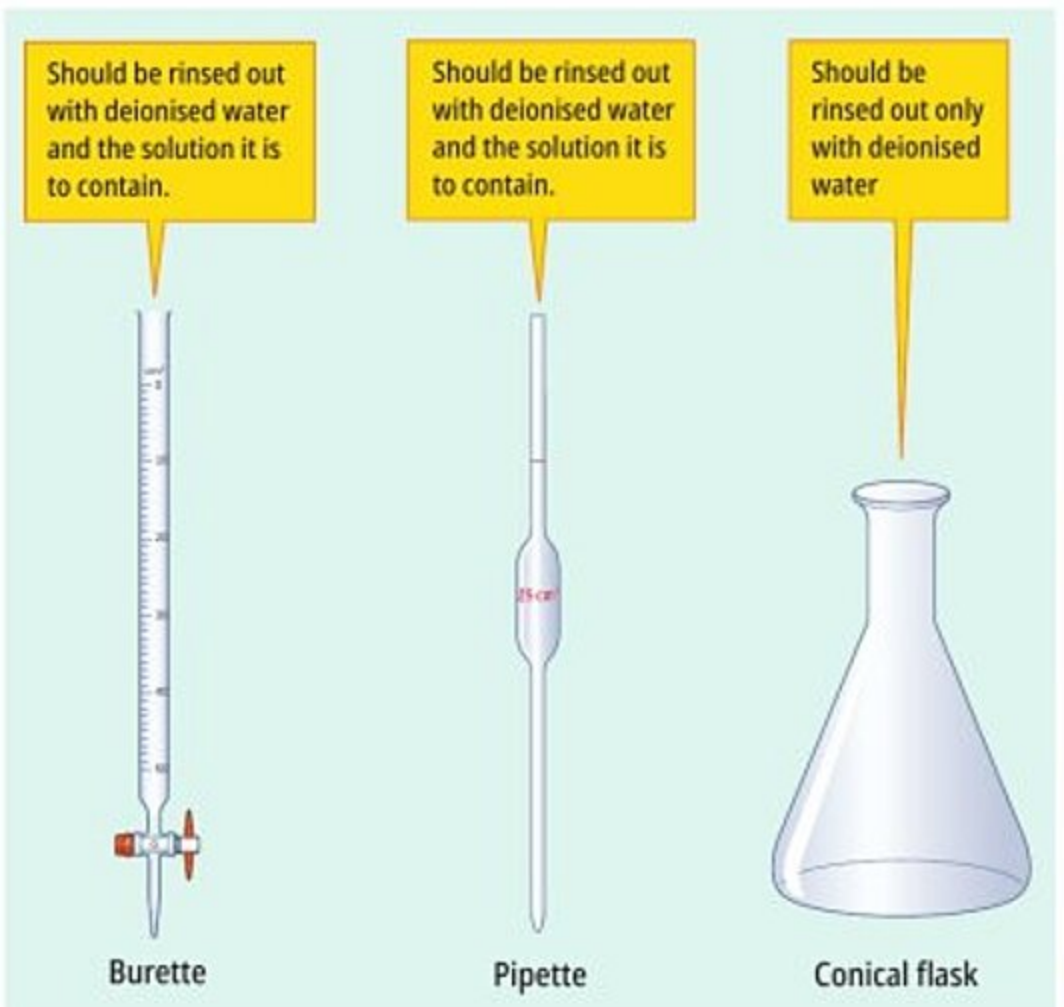

Should be rinsed out with deionised water and the solution it is to contain.
Should be rinsed out with deionised water and the solution it is to contain.
Should be rinsed out only with deionised water
Burette
Pipette
Conical flask

Figure 16.2 Summary of rinsing required when using a burette, pipette and conical flask in volumetric analysis.

Figure 16.3 A systematic error arises if the end point is always overshot due to lack of knowledge about the correct colour change at the end point.

Example 16.4

Question

A student performs a titration three times. The rough titration figure was 22.4 cm^3, the second titration figure was 22.2 cm^3 and the third titration figure was 22.1 cm^3. The true end point is 22.5 cm^3.

Question

(a) Is there evidence of a systematic error in carrying out the titration?

Answer

Yes, there is a systematic error, as all the values are consistently lower than the true value of 22.5 cm^3.

Question

(b) Is there evidence of a random error in carrying out the titration?

Answer

There is no evidence of a random error, as two results were obtained which agree to within 0.1 cm^3.

TEST YOURSELF: Attempt Questions 16.6 and W16.6–W16.11.

Summary What I should know

- Volumetric problems may be solved from first principle and also with the aid of key formulas.
- Number of moles = $\frac{\text{Mass (in grams)}}{\text{Relative molecular mass}}$
- Number of moles = $\frac{\text{volume}^* \times \text{molarity}}{1000}$
  (*in cm^3)
- $\frac{V_o \times M_o}{n_o} = \frac{V_r \times M_{red}}{n_r}$
- A systematic error is a consistent, repeating error that always occurs in one direction, i.e. it is always higher or always lower than the true value.
- A random error is an unpredictable fluctuation in a measurement around the true value that occurs due to variations in experimental conditions and procedures.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the terms *random error* and *systematic error*.	⬡	⬡	⬡
Discuss methods of minimising systematic and random errors in volumetric analysis.	⬡	⬡	⬡
Solve oxidation–reduction volumetric problems from first principles and using key formulas.	⬡	⬡	⬡

Chapter review questions

When answering these questions, use the values of relative atomic masses found in the *Formulae and Tables* booklet of the State Examinations Commission.

16.1 Ammonium iron(II) sulfate crystals are used in lawn feed.

To analyse the iron(II) content of ammonium iron(II) sulfate crystals, 11.76 g of the crystals were used to make up 250 cm^3 of solution. The ammonium iron(II) sulfate crystals were first dissolved in about 30 cm^3 of dilute sulfuric acid in a small beaker. This solution was then carefully transferred to a 250 cm^3 volumetric flask and the solution was made up to the mark using deionised water.

The resulting iron(II) solution was measured in 25.0 cm^3 portions into a conical flask, about 15 cm^3 of dilute sulfuric acid were added and the mixture was then titrated with a previously standardised 0.020 M solution of potassium manganate(VII) ($KMnO_4$).

(a) How could you ensure that all the solution was transferred from the small beaker to the volumetric flask?

(b) Describe the procedure for washing and filling a burette with the potassium manganate(VII) solution.

(c) Why was dilute sulfuric acid added to the iron(II) solution in the conical flask before the titrations were commenced?

(d) How was the end point detected?

The titration reaction is described by the equation:

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(e) In the titrations, 25.0 cm^3 portions of the iron(II) solution made from the crystals required 30.0 cm^3 of the 0.020 M $KMnO_4$ solution for complete reaction.

Calculate:

(i) The concentration of the solution in the volumetric flask in moles per litre of iron(II)

(ii) The mass of iron(II) in the 11.76 g of crystals used to make up the 250 cm^3 of solution

(iii) The percentage by mass of iron(II) in the crystals.

[LCH]

16.2 To determine the mass of iron in an iron tablet, four iron tablets of total mass of 1.26 g were dissolved and made up to 250 cm^3 of solution in a volumetric flask using dilute sulfuric acid and deionised water. About 20 cm^3 of dilute sulfuric acid were added to a conical flask containing 20 cm^3 portions of this iron (II) solution and the mixture then titrated with a 0.005 M solution of potassium manganate (VII), $KMnO_4$. The average titration value was 27.6 cm^3 of potassium manganate (VII), $KMnO_4$.

The balanced equation for the titration reaction is:

$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Calculate:

(i) The number of moles in 27.6 cm^3 of the potassium permanganate solution

(ii) The number of moles of iron (II) solution required to reduce this quantity of potassium permanganate

(iii) The (a) mass and (b) percentage of iron in each tablet.

16.3 A 5.00 g sample of impure iron was dissolved in dilute sulfuric acid and made up to 250 cm^3 in a volumetric flask. A 25.0 cm^3 portion of this solution was added to a conical flask and titrated with 0.025 M $KMnO_4$ and 24.0 cm^3 were required for complete reaction. The equation for the reaction is:

$MnO_4^- + 5Fe^{2+} + 8H^+ \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

(a) Why is a conical flask preferable to a beaker when performing a titration?

(b) State two operations carried out on the conical flask during the titration.

(c) Calculate the concentration in moles per litre of Fe^{2+} in the solution.

(d) Determine the percentage purity of the iron sample.

Chapter review questions

16.4 A 0.1 M solution of sodium thiosulfate was prepared by weighing out a certain mass of crystalline sodium thiosulfate ($Na_2S_2O_3.5H_2O$) on a clock glass, dissolving it in deionised water and making the solution up to the mark in a volumetric flask. A burette was rinsed and then filled with this solution and it was titrated against 20.0 cm^3 portions of a previously standardised iodine solution in a conical flask. The average titre was 14.9 cm^3.

The balanced equation for the titration reaction is:

$$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$$

Calculate:

(i) The number of moles of sodium thiosulfate in the 14.9 cm^3 used in the titration

(ii) The number of moles of I_2 that reacted with this number of moles of sodium thiosulfate

(iii) Find the concentration of the I_2 solution in (a) moles per litre, (b) grams per litre.

Figure 16.5

16.5 **(a)** The container shown in Figure 16.5 is labelled sodium thiosulfate pentahydrate. Explain the term *pentahydrate*.

(b) To determine the concentration of a solution of iodine (I_2), 25 cm^3 of the solution was titrated against a solution of 0.12 M sodium thiosulfate. The average titration figure was 21.15 cm^3.

$$I_2 + 2S_2O_3^{2-} \rightarrow 2I^- + S_4O_6^{2-}$$

Calculate:

(i) The number of moles of sodium thiosulfate in the 21.15 cm^3 used in the titration

(ii) The number of moles of I_2 that reacted with this number of moles of sodium thiosulfate

(iii) The concentration of the I_2 solution in (a) moles per litre, (b) grams per litre.

16.6 **(i)** Distinguish between the terms *systematic error* and *random error.*

(ii) A student carries out an experiment to measure the amount of elemental iron in an iron tablet. Describe one example of a systematic error and one example of a random error that could arise in this experiment.

(iii) For each example given in (ii), describe how this source of error could be addressed.

(iv) Explain how random and systematic errors differ in terms of their effect on the accuracy and precision of results obtained.

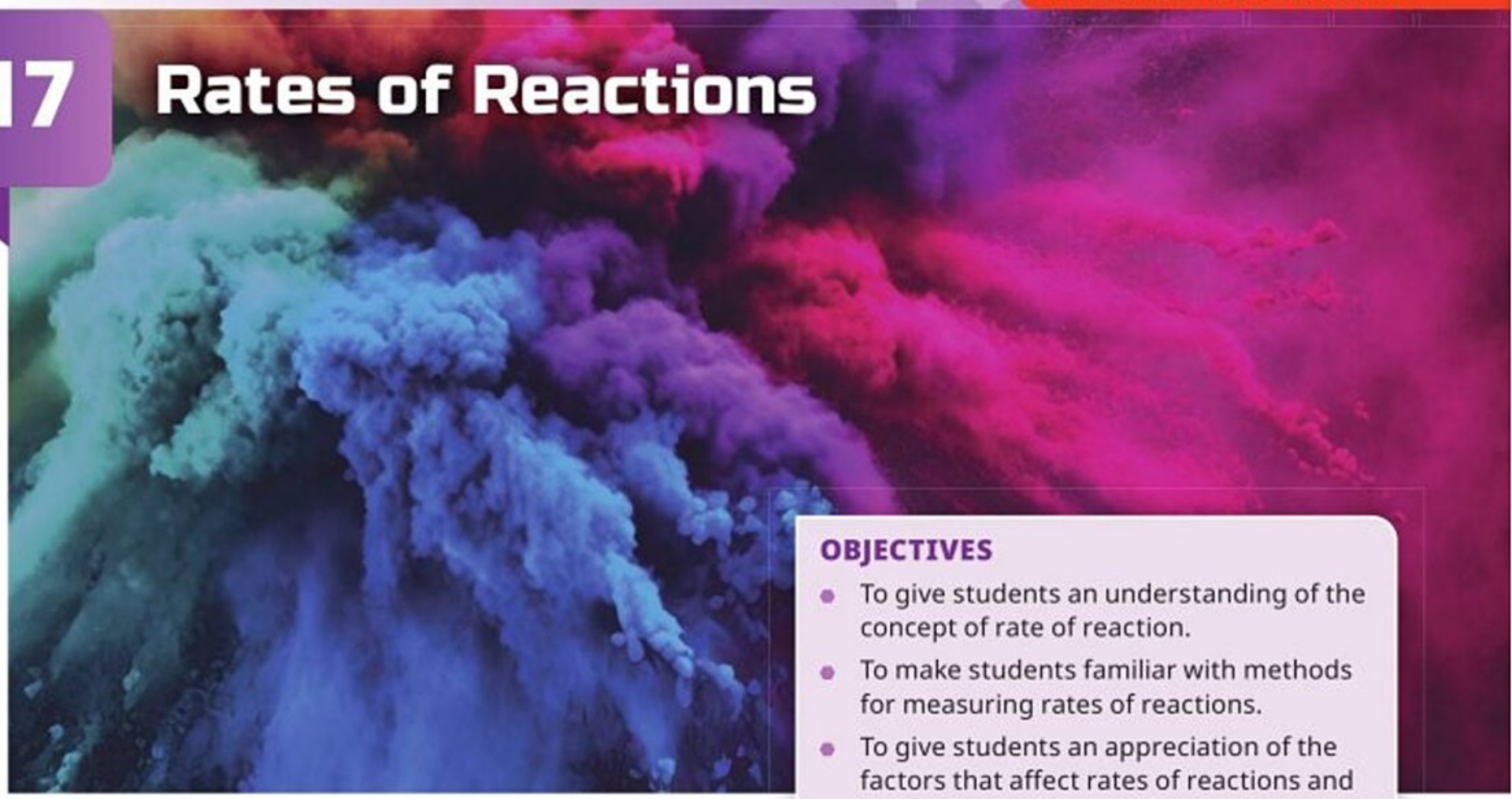
(v) A student carries out a titration and consistently records an end point that is 0.2 cm^3 too high. What type of error is this? Give one possible cause of this error.

(vi) State two ways of reducing sources of random errors when carrying out a titration.

(vii) Explain why systematic errors remain, even if an experiment is repeated several times.

(viii) Describe the correct rinsing procedures that are necessary when preparing a pipette, burette and a conical flask for use in titrations. Explain the errors that will arise if these rinsing techniques are not carried out correctly.

17 Rates of Reactions



OBJECTIVES

- To give students an understanding of the concept of rate of reaction.
- To make students familiar with methods for measuring rates of reactions.
- To give students an appreciation of the factors that affect rates of reactions and can interpret graphs related to rates of reactions.
- To ensure that students understand the mechanisms of catalysis.

17.1 Introduction

Chemical reactions occur at different speeds. If a lighted taper is put near a balloon filled with hydrogen, a chemical reaction takes place very quickly and a loud bang is heard. This reaction is extremely fast. Explosions are usually extremely fast reactions in which a large volume of gas is produced in a very short period of time. Another example of a very fast react is the inflation of the air bag in a car when a crash takes place, Figure 17.1 The chemical reaction that occurs takes place in a fraction of a second, releasing nitrogen gas to inflate the air bag. (We will study this reaction in more detail in the *Assessment and Exam Guide*.)

Figure 17.1 The chemical reaction that inflates an air bag occurs in a fraction of a second.

On the other hand, other chemical reactions can take weeks, months or years to take place, Table 17.1.

Reaction type	Typical time to take place
Rusting of iron	Days to years
Formation of fossil fuels	Millions of years
Decomposition of non-biodegradable plastics	Hundreds to thousands of years
Decomposition of biodegradable plastics	Months to a few years
Ripening of fruit	Days to a few weeks

Table 17.1 Some examples of chemical reactions that take place slowly

- It is important for chemists to know how quickly a particular chemical reaction occurs and how to change the speed of the reaction.
- If a chemical reaction is being used in an industrial process, economic problems may arise if the reaction occurs too slowly.

In this chapter, we will study the factors that affect the speed at which reactions occur and will also look at the theory used by chemists to explain the results of many experiments carried out in this area of chemistry.

17.2 Reaction rate

We use the word 'rate' a lot in our everyday lives. You may have heard the word 'rate' used to describe the speed of a car. Speed is a rate. For example, a car may be travelling at 60 km per hour, i.e. its rate of change of distance with time is 60 km per hour. Speed is calculated by dividing the distance travelled by the time taken for the car to travel that distance.

$$\text{Speed} = \text{Rate of change of distance with time} = \frac{\text{Distance travelled}}{\text{Time taken}}$$

Thus, a car that travels 200 km in 4 hours has an average speed of 50 km per hour.

We talk about heart rate – how many times your heart beats per minute. For example, if you are resting, your heart rate might be 70 beats per minute. We refer to the growth rate of a plant – the increase in height over a year (5 cm/year).

So, whenever we use the word 'rate', we are always measuring change over time. Chemists use the term ***rate of reaction*** to describe how quickly chemical changes occur.

The **rate of reaction** is defined as the change in concentration per unit time of any one reactant or product.

- Chemists measure the rate of a chemical reaction by measuring how the concentration of any one reactant or product changes with time.
- For example, if a chemical reaction produces a gas, the rate of reaction may be calculated by dividing the volume of gas produced by the time taken to produce that particular volume.

For example, when hydrogen peroxide decomposes to give off oxygen gas, the rate of the reaction may be found by measuring the volume of oxygen given off as the reaction proceeds. This experiment is studied in the next section.

17.3 Measuring rates of reactions

A balanced chemical equation does not give us any information about how quickly a reaction takes place. To measure the rate of a reaction, we must carry out laboratory practical work. In this section, we will investigate how chemists measure rates of reactions in the laboratory. We first consider a reaction that can be monitored by collecting the gas evolved in the reaction.

17.1 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 14 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 14

To investigate the rate of decomposition of hydrogen peroxide using manganese dioxide as a catalyst

Introduction

In this experiment, we will investigate the rate at which oxygen is released from a sample of hydrogen peroxide. Hydrogen peroxide decomposes slowly into oxygen and water. However, the rate at which it decomposes may be increased by adding a small amount of manganese dioxide. Manganese dioxide is a black powder that acts as a catalyst to speed up the decomposition of the hydrogen peroxide.

$$H_2O_2 \xrightarrow{MnO_2} H_2O + \tfrac{1}{2} O_2$$

Key steps in procedure

- Dilute hydrogen peroxide solution is placed in a conical flask.
- A delivery tube is connected to an inverted graduated cylinder filled with water and standing in a basin of water, Figure 17.2(a).

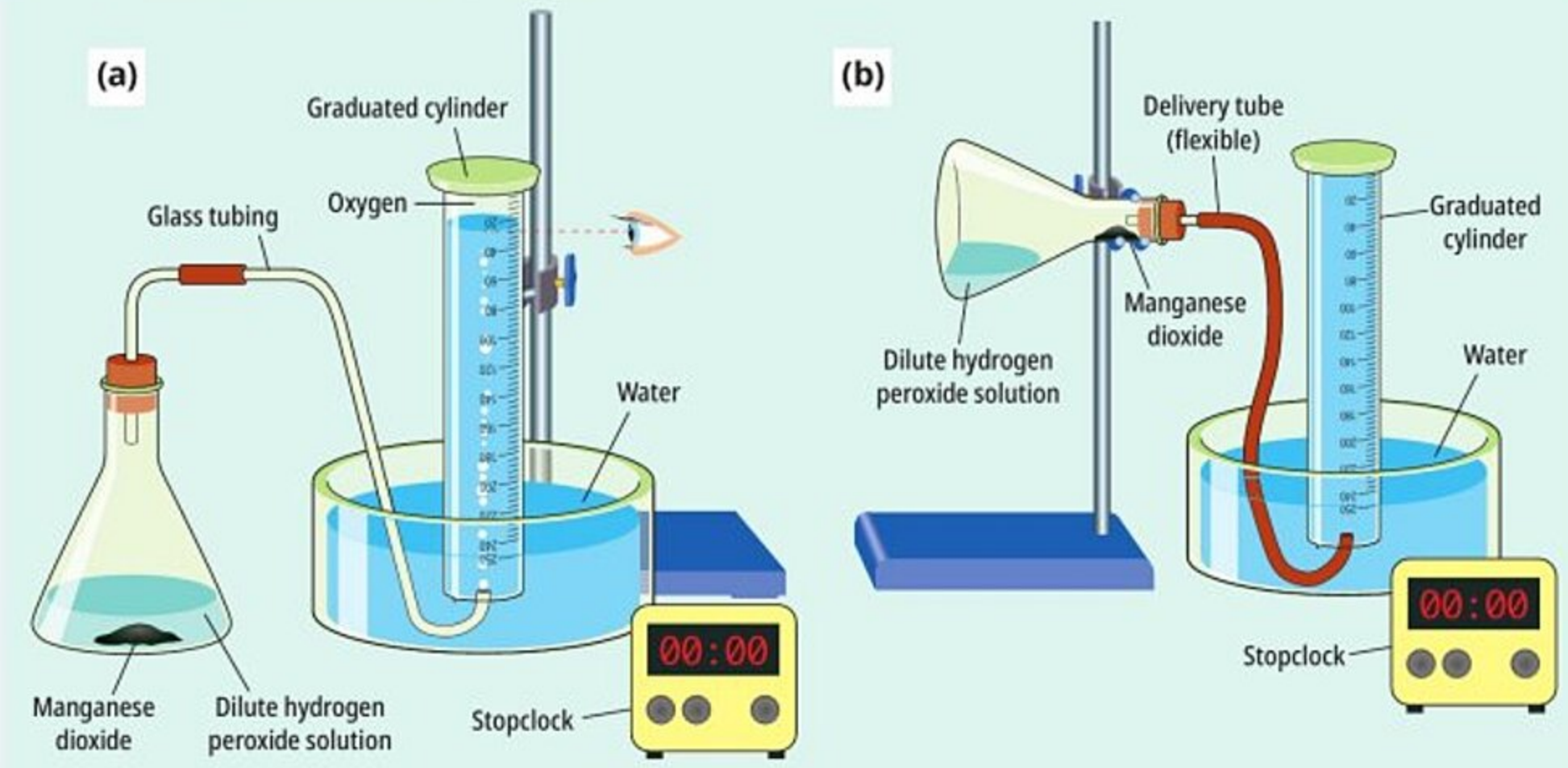


Figure 17.2 Apparatus to monitor the rate of decomposition of hydrogen peroxide. In method (a) the manganese dioxide is added directly to the hydrogen peroxide, and in method (b) the conical flask is lowered into the vertical position to start the reaction.

- At the beginning of the experiment (zero time), a small amount of manganese dioxide is quickly added to the hydrogen peroxide in the conical flask, the rubber stopper is immediately inserted in the conical flask and the stopwatch is immediately started. The mixture is shaken briefly.
- An alternative way of carrying out the experiment is to use the apparatus as shown in Figure 17.2(b). The conical flask is lowered into the vertical position so that the manganese dioxide falls into the hydrogen peroxide and, at the same moment, the stopwatch is started. The mixture is shaken briefly.
- The volume of gas in the graduated cylinder is measured at regular intervals.
- The results are entered into a table.

Time (mins)	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Volume O_2 (cm^3)									

The volume of gas continues to be measured until the reaction is over, i.e. when the volume of gas evolved remains constant with time.

A graph of volume of oxygen (y-axis) against time (x-axis) is drawn on graph paper. A graph of similar shape to that in Figure 17.3 is obtained.

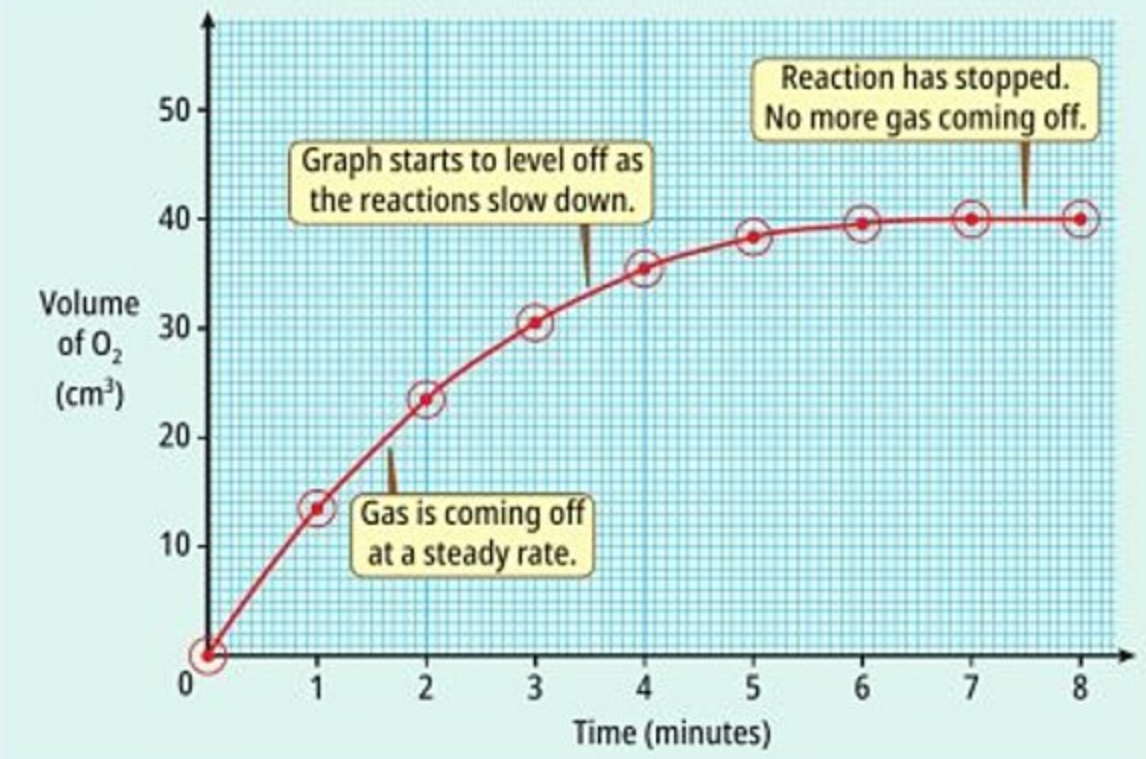


Figure 17.3 When the volume of oxygen given off is plotted against the time, a graph similar to this one is obtained.

The **average rate of reaction** is the overall change in the amount of reactant or product over a period of time. It tells you how fast a reaction is taking place as an average between two points in time.

Calculations from graph

It is easy to calculate the average rate of reaction from the graph.

For example, the **average rate** of evolution of oxygen is calculated from the formula:

$$\text{Average rate} = \frac{\text{Total volume of oxygen given off } (cm^3)}{\text{Total time for reaction to go to completion (min)}}$$

For example, from Figure 17.3 we see that the average rate $= \frac{40\ cm^3}{7\ mins} = 5.71\ cm^3/min$

Later on we will see how graphs of this type may be used for other types of calculations.

DIGITAL: A video of this experiment is available on FolensHIVE.

Note:

- When drawing this apparatus, do not forget to label the graduated cylinder and to draw graduation marks on it so that it does not look like a gas jar.

EXAM TIP!

If you are asked why the hydrogen peroxide should not be added to the manganese dioxide using a dropping funnel, explain that the method is incorrect, as it does not give an exact starting time for the reaction taking place. Also, the volume of gas collected would be incorrect due to displacement of air caused by adding the peroxide.

When carrying out the above experiment, we saw that the reaction proceeds quite rapidly at the beginning of the experiment and slows down later on. In this experiment, we have measured the **average rate** of production of oxygen gas. In measuring the average rate, we have divided the total volume of gas by the total time.

Measuring the average rate of production of a gas is similar to the use of average speed cameras to measure the average speed of a car, Figure 17.4.

Figure 17.4 Average speed cameras work in pairs. They measure the average speed by dividing the total distance travelled between the two cameras by the time taken to travel that distance.

- Two cameras are placed on a road a fixed distance apart.
- Each camera records the details of the car as it passes the camera.
- The system records how long it takes the car to travel the distance between the two cameras and then the system calculates the speed of the car.

$$\text{Average speed} = \frac{\text{Total distance}}{\text{Total time}}$$

If the average speed is above the legal speed limit, the driver is in trouble!

Figure 17.5 This Garda is more interested in measuring the instantaneous speed rather than the average speed of the car.

In some cases, the Gardaí measure the speed of a car at a particular instant in time. This is called the instantaneous speed, Figure 17.5. Similarly, in some cases chemists need to measure the rate of reaction at a particular instant in time. The rate of reaction at a particular instant in time is called the **instantaneous rate**. The method of measuring the instantaneous rate of reaction is shown in the following example.

The **instantaneous rate** of reaction is the rate of reaction at any one particular time during the reaction.

Example 17.1

Question

In an experiment, 25 cm^3 of 0.1 M sulfuric acid were added to excess granulated zinc in a reaction vessel. The hydrogen evolved in the reaction was collected and its volume (at room temperature and pressure) was measured at regular intervals of time. The results obtained are shown in the following table:

Time (mins)	0	1	2	3	4	5	6	7	8	9	10	11
Volume of hydrogen (cm^3)	0	30	45	52.5	56.3	58.2	60	61	61.5	62	62	62

Draw a labelled diagram of the apparatus you would use in this experiment. [LCH]

Answer

(i) The gas may be collected over water in a graduated cylinder or it may be collected in a gas syringe (Figure 17.6). When answering questions of this type, always ensure you label the diagram.

EXAM TIP!

A common error among students is to forget to show the graduation marks on the graduated cylinder. Therefore, the graduated cylinder could be mistaken for a gas jar.

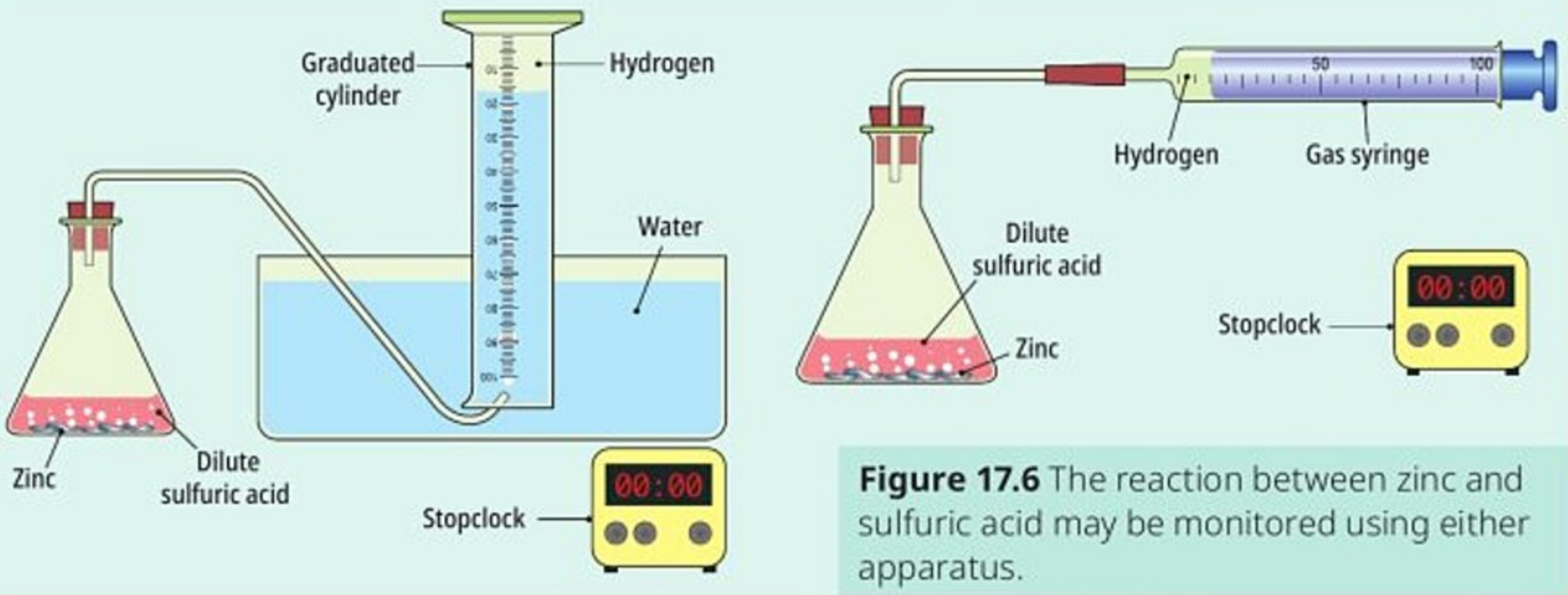


Figure 17.6 The reaction between zinc and sulfuric acid may be monitored using either apparatus.

Question

Plot on graph paper the results in the above table and comment on the shape of the graph.

Answer

The data are plotted in Figure 17.7.

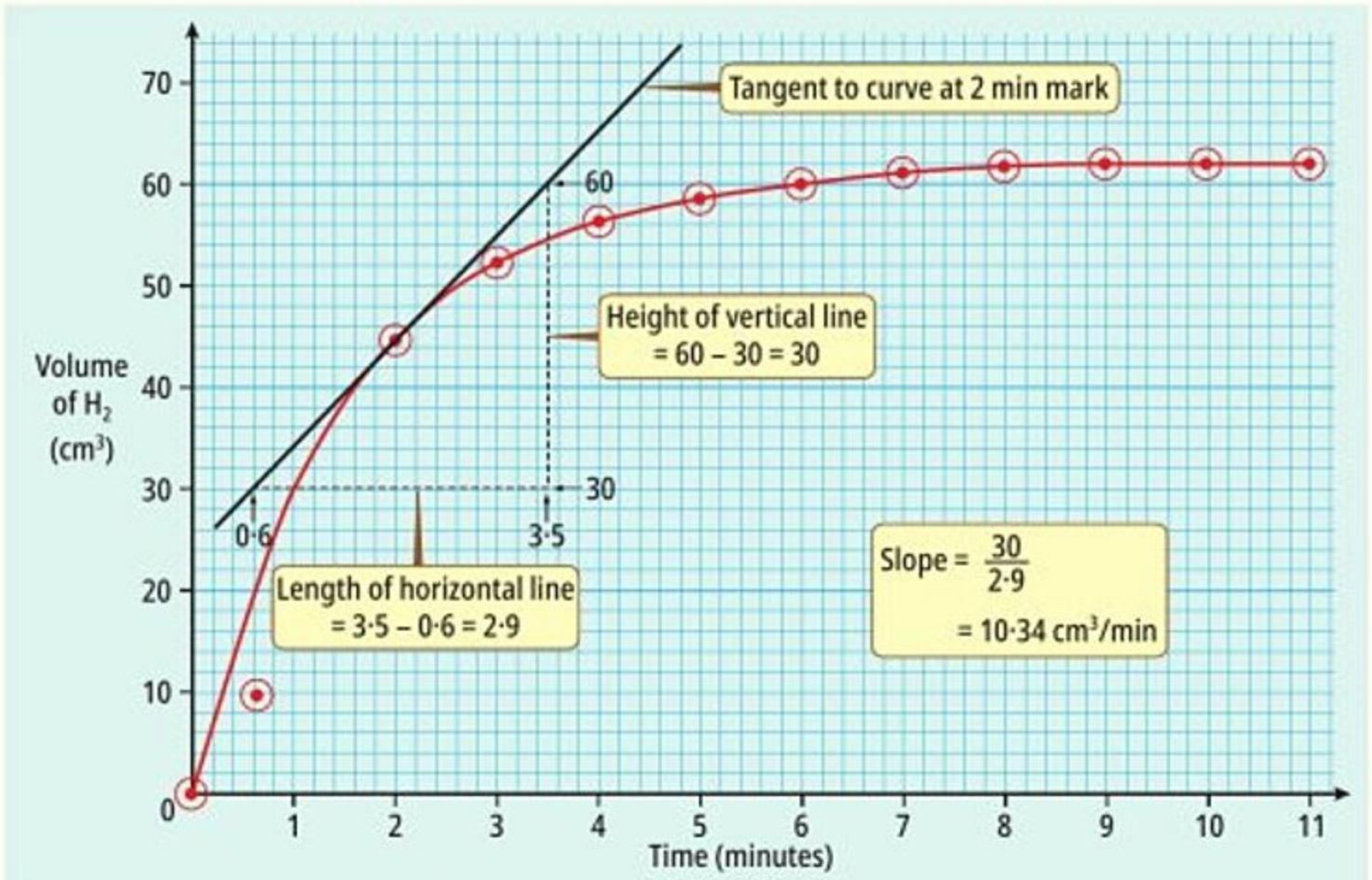


Figure 17.7 The results of the experiment are plotted on a graph.

- The shape of the graph tells us that the reaction is fairly fast initially – the graph rises steeply.
- The slope of the curve at the beginning of the experiment gives us a good measure of the initial reaction rate. The steeper the slope of the curve, the faster the rate.
- As time proceeds, the reaction becomes slower and slower, as indicated by the fact that the slope of the curve becomes less and less steep. The graph levels off when the reaction is over.

Question

Find, using the graph, the rate of reaction at two minutes, (i.e. the instantaneous rate) expressing the rate in terms of cm^3 of hydrogen liberated per minute.

Answer

- To measure the instantaneous rate at two minutes, we must measure the slope of the tangent to the curve at the 2-minute mark on the graph. Think of the instantaneous rate at 2 minutes as being like a snapshot of the speed of the reaction at the 2-minute mark.
- The slope of the tangent at the 2-minute mark tells us the rate of production of hydrogen at that instant in time. To measure the slope of the line, draw a tangent at the 2-minute mark on the graph and then draw any vertical line and any horizontal line as shown in Figure 17.7.
- The slope of the line is then the length of the vertical line divided by the length of the horizontal line.

$$\text{Instantaneous rate at 2 mins} = \text{Slope of line} = \frac{\text{Change in volume}}{\text{Change in time}} = \frac{30\ cm^3}{2.9\ min} = 10.34\ cm^3/min.$$

EXAM TIP!

A slight variation in the value of the slope is always obtained depending on where you draw the vertical and horizontal lines. This variation is always taken into account in exam questions. As a general 'rule of thumb', choose points on the tangent at least half a unit of time on the right and half a unit of time on the left of the given time, e.g. in the above example, the vertical line should begin at some time **after** 2.5 minutes and the horizontal line some time **before** 1.5 minutes.

Measuring the initial rate of reaction

The initial rate shows how fast the reaction starts when the concentrations of the reactants are at their maximum.

Chemical reactions usually takes place at their fastest at the beginning of the reaction. We will see in the next section that concentration affects the rate of reaction. The concentration of the reactants is highest at the beginning, since the reactants are only about to start being used up in the reaction.

The **initial rate** of reaction is the rate of reaction at the beginning of the reaction, i.e. just after the reactants are mixed at time t = 0.

To measure the initial rate of reaction, you need to draw a tangent to the curve at the (0,0) mark. As shown in Figure 17.8, the slope of the tangent is a measure of the initial rate.

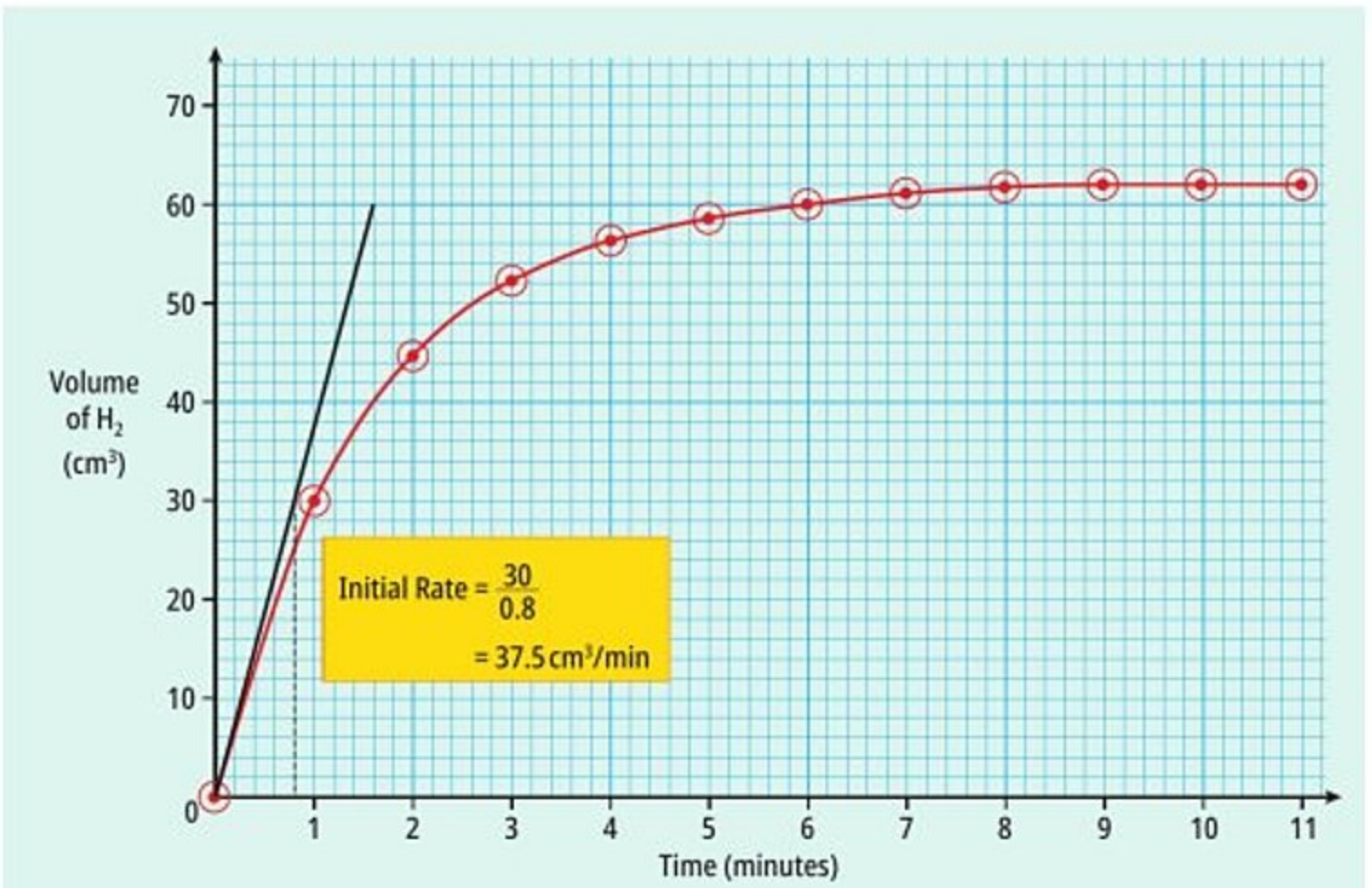


Figure 17.8 The initial rate is measured by drawing a tangent to the curve at the (0,0) mark.

$$\text{Initial rate at 0 mins} = \text{Slope of line} = \frac{\text{Change in volume}}{\text{Change in time}} = \frac{30\ \text{cm}^3}{0.8\ \text{min}} = 37.5\ \text{cm}^3/\text{min}.$$

If a tangent is not drawn and you wish to get a rough estimate of the initial rate of reaction, you could estimate the initial rate by taking a small time interval near the beginning of the reaction and measuring the average rate over this short time interval. For example, after 0.4 minutes a volume of 12 cm^3 of H_2 has been produced.

$$\text{Therefore, average rate} = \frac{12\ \text{cm}^3}{0.4\ \text{min}} = 30\ \text{cm}^3/\text{min}$$

17.4 Factors affecting rates of reactions

By experiment it is found that the rate of a reaction depends on six factors which we will now study.

(i) Nature of reactants

The main points concerning the effect of the nature of reactants on the rate of reaction may be summarised as follows:

- Covalent compounds are typically slower to react when compared to ionic compounds. This is because covalent bonds must be broken before they can react, whereas ions are dissociated already and can react immediately.
- You may recall that when carrying out experiments to test for the presence of various anions in solution (Chapter 5), we found that all of the precipitation reactions were instantaneous, i.e. a precipitate was immediately formed on mixing the reagents. For example, on adding a solution containing some Ag^+ ions to a solution containing Cl^- ions, a white precipitate was formed immediately. The reason why the reaction takes place so quickly is because all that is involved is simply the coming together of oppositely charged ions.

$$Ag^+ + Cl^- \rightarrow AgCl\downarrow$$

- No energy was needed to break any bonds, since the Ag^+ ions and Cl^- ions already existed as free ions in the solutions.
- Consider the reaction shown in Figure 17.9.
- In the first test-tube, a solution of bromine in water is added to a liquid called hexane and a stopwatch started. Bromine and hexane react as follows:

C_6H_{14}	+	Br_2	→	$C_6H_{13}Br$	+	HBr
hexane (colourless)		bromine (red)		bromohexane (colourless)		hydrogen bromide (colourless)

The products of the reaction are all colourless. Therefore, we know that the reaction is over when the red colour of the bromine disappears. The stopwatch is started as soon as the bromine solution is added to the hexane. It takes over sixteen minutes for the colour to disappear completely. Both hexane and bromine are covalent compounds. It takes time for covalent bonds to be broken and new covalent bonds to be formed. Therefore, the reaction is slow.

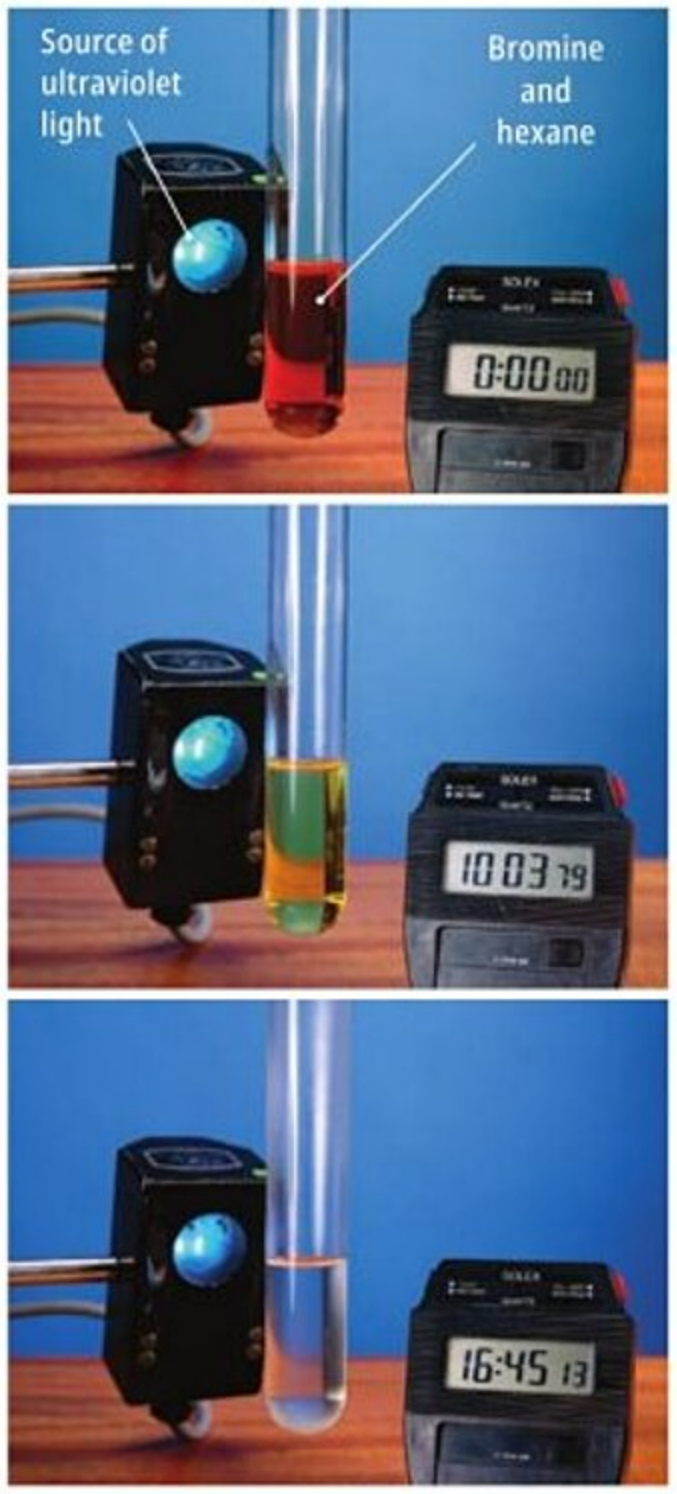


Figure 17.9 It takes over 16 minutes for the bromine to fully react with the hexane. Reactions that involve breaking of covalent bonds usually take longer compared to reactions that merely involve ions coming together.

Conclusions

- Reactions that do not involve bond breaking but merely the coming together of oppositely-charged ions in solution are usually fast at room temperature.
- Reactions that involve breaking of covalent bonds are usually slow at room temperature.

(ii) Surface area

When potatoes are being cooked in boiling water, a chemical reaction occurs. One way of increasing the rate at which the potatoes cook is to cut them into smaller pieces. Similarly, it is easier to light a fire using small pieces of wood rather than a large log.

The effect of surface area on reaction rates may be easily demonstrated in the laboratory. Large lumps of marble (calcium carbonate) react slowly with dilute hydrochloric acid to release carbon dioxide, Figure 17.10. However, if the same volume of the dilute hydrochloric acid is added to the same mass of small lumps calcium carbonate at the same temperature, there is a very large increase in the rate.

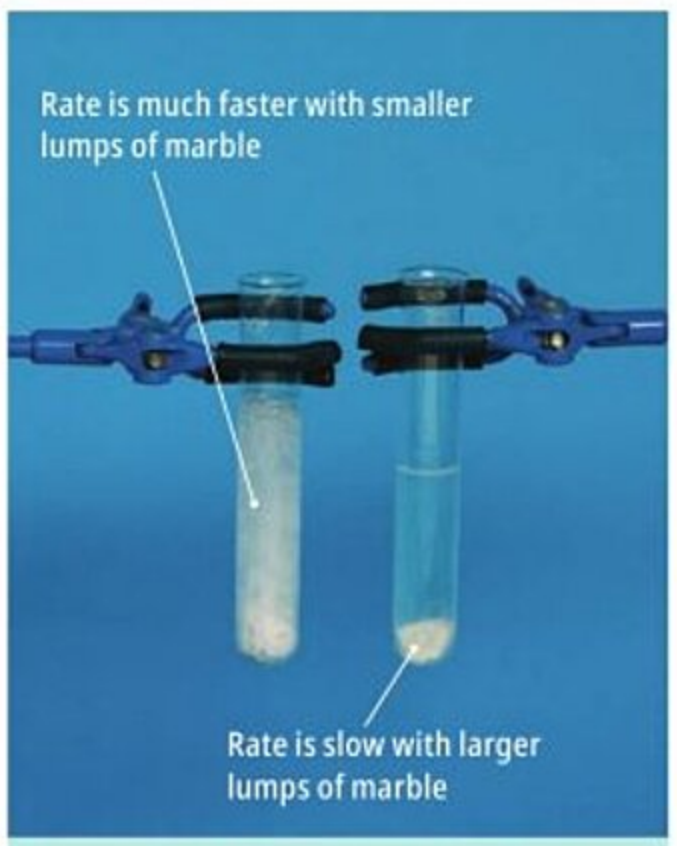


Figure 17.10 Large lumps of marble react with the hydrochloric acid to give off bubbles of carbon dioxide at a steady rate. Smaller lumps react at a much faster rate.

17.2 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 15 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 15

To investigate the effect of surface area (particle size) on the rate of reaction between calcium carbonate and hydrochloric acid

In this experiment, we will investigate the rate at which carbon dioxide is given off in the reaction between marble chips (calcium carbonate) and dilute hydrochloric acid. Since carbon dioxide dissolves in water, the rate of reaction is not measured by collection over water. Instead, the rate is measured by studying the loss in mass due to carbon dioxide being evolved.

$$\underset{\text{calcium carbonate}}{CaCO_3} + \underset{\text{hydrochloric acid}}{2HCl} \rightarrow \underset{\text{calcium chloride}}{CaCl_2} + \underset{\text{water}}{H_2O} + \underset{\text{carbon dioxide}}{CO_2}$$

Key steps in procedure

- A conical flask containing about 20 g of **large** marble chips and a graduated cylinder containing about 50 cm^3 of dilute hydrochloric acid are placed on the pan of the electronic balance, Figure 17.11. A cotton wool plug is placed in the mouth of the conical flask to prevent any loss of spray during the experiment while allowing the carbon dioxide gas to escape.
- The total mass is read from the balance.
- The dilute hydrochloric acid is then added to the conical flask with swirling, the cotton wool plug is replaced, the stopwatch is started, and the conical flask and graduated cylinder are replaced on the balance.

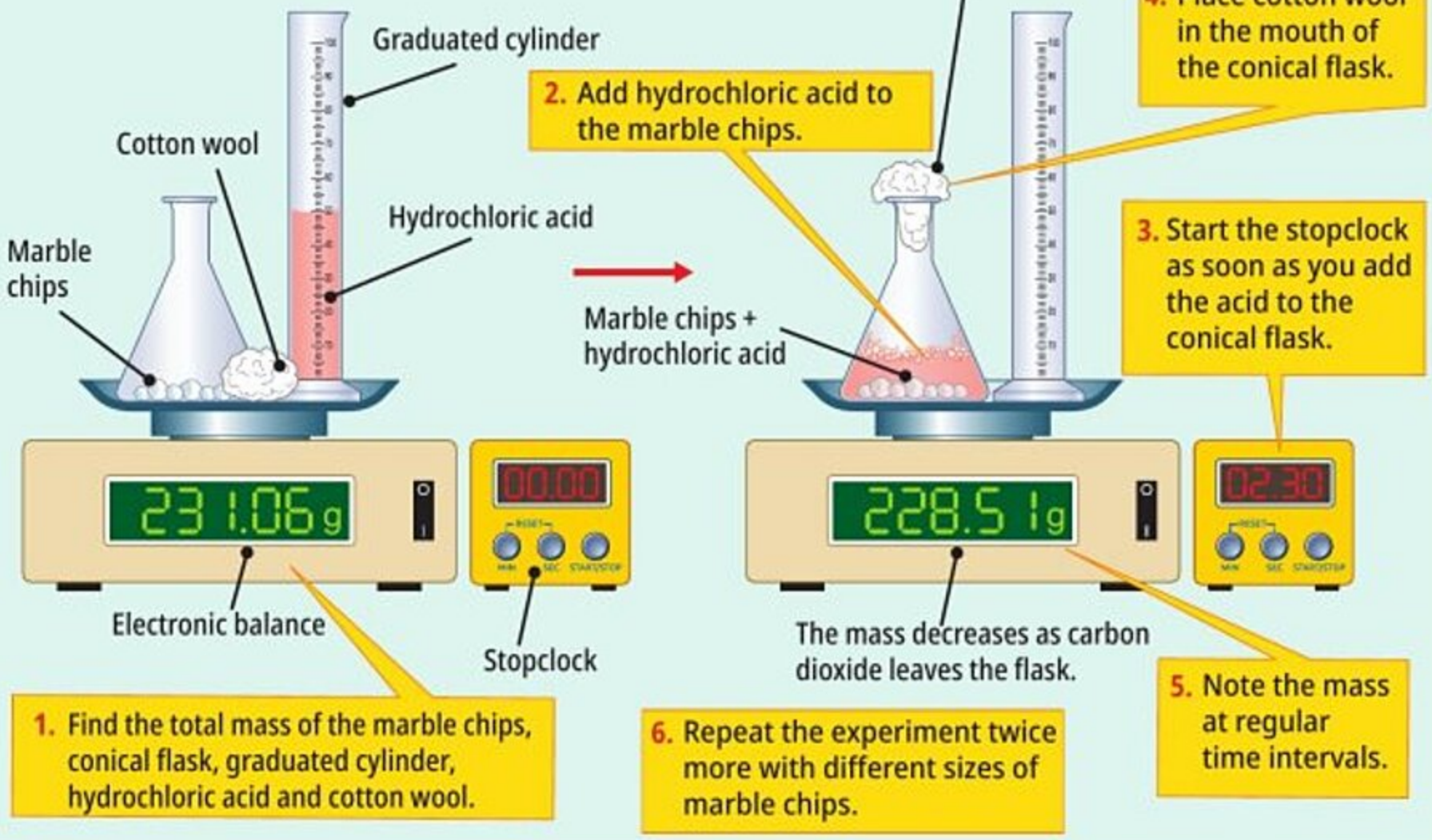

Carbon dioxide diffuses out of the flask. The spray is prevented from escaping by the cotton wool.
Graduated cylinder
Cotton wool
Hydrochloric acid
Marble chips
231.06 g
00:00
Electronic balance
Stopclock
1. Find the total mass of the marble chips, conical flask, graduated cylinder, hydrochloric acid and cotton wool.
2. Add hydrochloric acid to the marble chips.
Marble chips + hydrochloric acid
4. Place cotton wool in the mouth of the conical flask.
3. Start the stopclock as soon as you add the acid to the conical flask.
228.51 g
02:30
The mass decreases as carbon dioxide leaves the flask.
5. Note the mass at regular time intervals.
6. Repeat the experiment twice more with different sizes of marble chips.

Figure 17.11 Apparatus to study the effect of surface area (particle size) on the rate of reaction. As the hydrochloric acid reacts with the marble chips, there is a loss in mass as carbon dioxide is given off and escapes from the conical flask.

- The mass is recorded every 30 seconds for about 10 minutes.
- The loss in mass is due to the fact that the carbon dioxide escapes through the cotton wool plug.
- The cotton wool plug prevents any loss of mass due to the escape of the acid spray formed as the marble reacts with the hydrochloric acid. The results are summarised in the form of a table.

Time (mins)	0	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0
Total mass (g)									
Loss in mass (g)									

- The loss in mass is calculated by subtracting each value of the mass from the initial mass before the reaction began.
- The experiment is repeated with 20 g of **small** marble chips, keeping all other conditions the same.
- It is found that the rate of loss of carbon dioxide is greatly increased with the smaller-sized chips.

Calculations from graph

A graph of mass against time will give a graph similar to that shown in Figure 17.12.

Alternatively, a graph of loss in mass against time will give a graph similar to that shown in Figure 17.13.

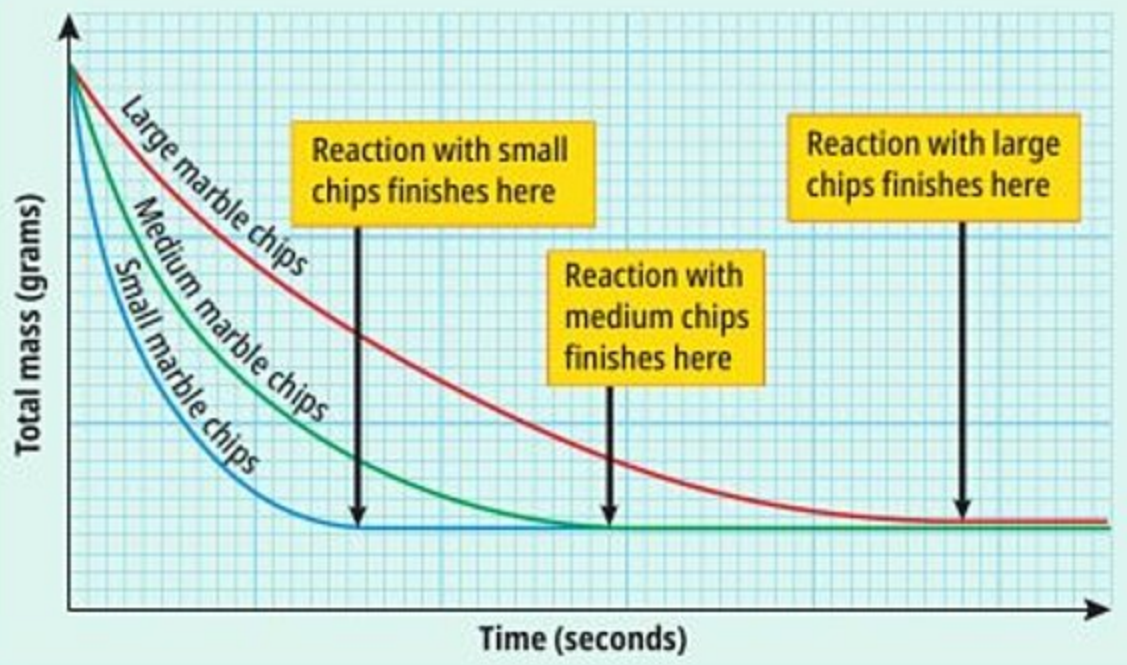

Large marble chips
Medium marble chips
Small marble chips
Reaction with small chips finishes here
Reaction with medium chips finishes here
Reaction with large chips finishes here
Total mass (grams)
Time (seconds)

Figure 17.12 The rate of reaction increases as the surface area of the marble chips increases. In other words, the smaller the marble chips, the faster the rate.

The **greater** the surface area, the **faster** the rate of reaction. In other words, the **smaller** the particle size, the **faster** the rate.

DIGITAL: A video of this experiment is available on FolensHIVE.

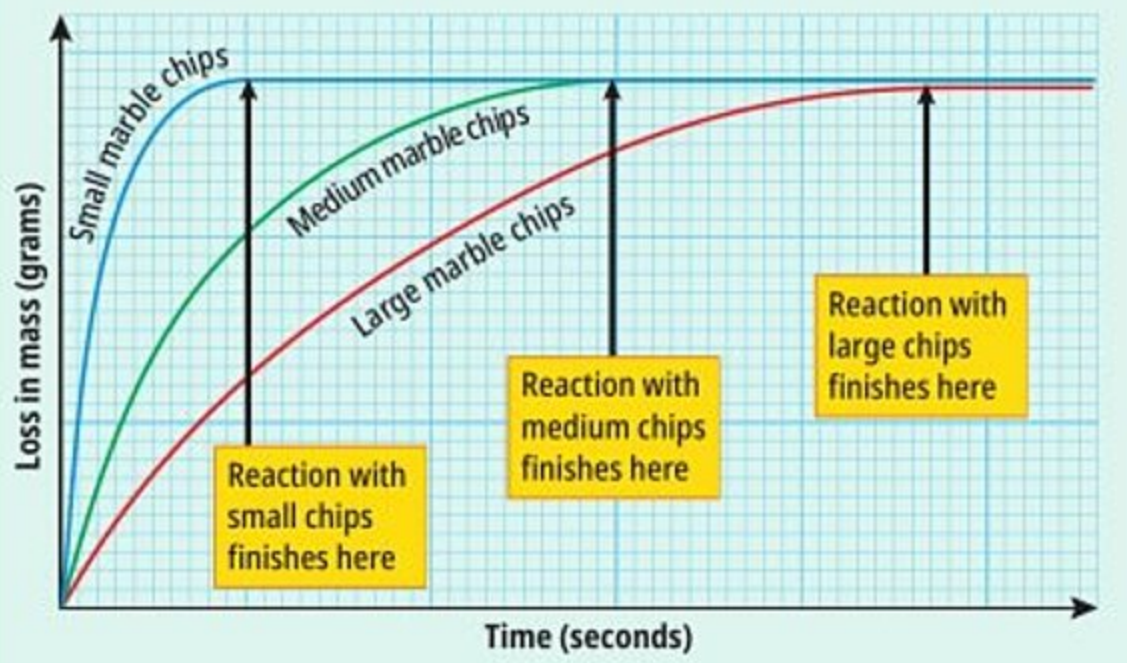

Small marble chips
Medium marble chips
Large marble chips
Reaction with small chips finishes here
Reaction with medium chips finishes here
Reaction with large chips finishes here
Loss in mass (grams)
Time (seconds)

Figure 17.13 The rate of loss of mass increases as the surface area of the marble chips increases. In other words, the smaller the marble chips the faster the rate of loss of carbon dioxide.

Dust explosions

Figure 17.14 The results of a dust explosion in a sugar plant in the USA.

One of the big problems when dealing with very finely divided particles is that a 'dust explosion' may occur. This is a particular problem in flour mills, grain silos and coal mines. In these cases a build-up of very fine dust in the air can lead to an explosive reaction taking place, Figure 17.14.

A controlled dust explosion may be demonstrated in the laboratory using a very fine powder called lycopodium powder (a type of pollen). The lycopodium powder is blown over a candle in a large coffee tin on which the lid has been firmly placed, Figure 17.15.

Note from Figure 17.15 that there are several conditions needed for a dust explosion to occur:

1. The explosion must take place in an enclosed space.
2. The particles must be combustible, i.e. they must burn.
3. There must be a source of ignition, i.e. something such as a flame or spark to ignite the dust particles.
4. The particles must be dry.
5. There must be oxygen (air) present.

When a dust explosion takes place in a coffee tin, the force of the explosion is sufficient to blow the lid high into the air, Figure 17.16.

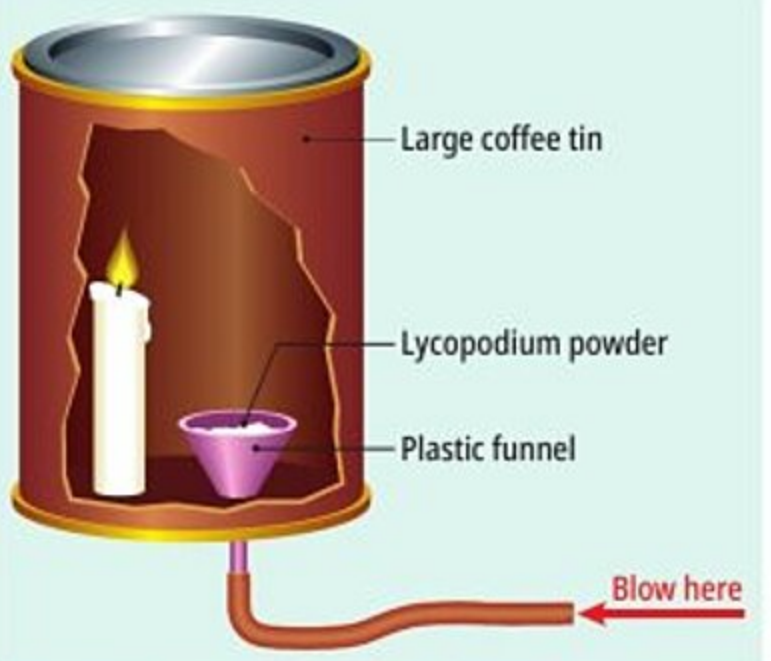


Figure 17.15 Experiment to illustrate the fact that materials in a powdered state undergo very fast reactions.

Figure 17.16 The lycopodium bomb works very well! The top of the lid was blown off by the dust explosion that took place inside the tin.

(iii) Concentration

- By experiment it is found that changing the concentrations of the reactants in a chemical reaction alters the rate of the reaction.
- The more concentrated the reactants, the faster the rate of reaction.
- This explains why the initial rate of reaction is usually much greater than the average rate of reaction.

For example, consider the reaction in which magnesium metal reacts with hydrochloric acid.

$$\underset{\text{magnesium}}{Mg} + \underset{\text{hydrochloric acid}}{2HCl} \rightarrow \underset{\text{magnesium chloride}}{MgCl_2} + \underset{\text{hydrogen}}{H_2}$$

Suppose that we react 0.1 g of magnesium with 50 cm^3 of 1.5 M HCl in the apparatus shown in Figure 17.17. In this experiment, the hydrochloric acid is in excess so that the reaction comes to an end when the magnesium metal is used up. The volume of gas evolved is measured at regular intervals. When the reaction stops, the flask is washed out, and the experiment repeated with 50 cm^3 of less concentrated acid, e.g. 1.0 M HCl and 0.5 M HCl.

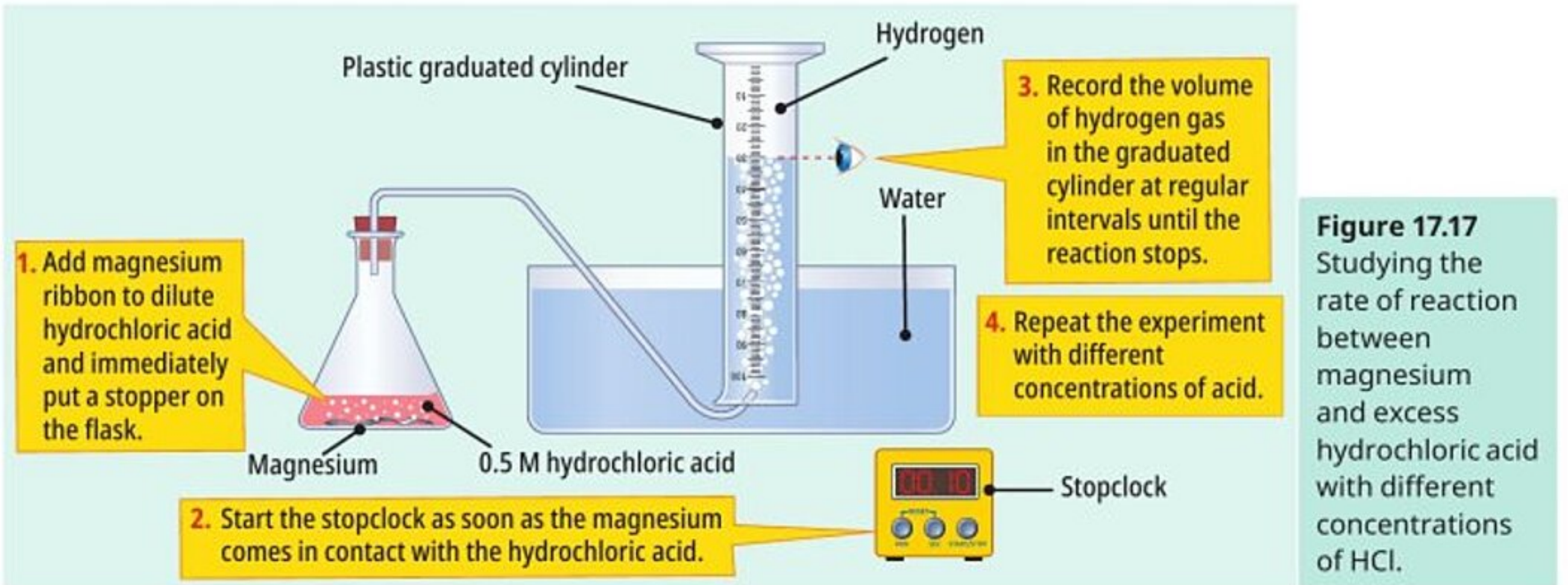

Hydrogen
Plastic graduated cylinder
3. Record the volume of hydrogen gas in the graduated cylinder at regular intervals until the reaction stops.
Water
1. Add magnesium ribbon to dilute hydrochloric acid and immediately put a stopper on the flask.
4. Repeat the experiment with different concentrations of acid.
Magnesium
0.5 M hydrochloric acid
Stopclock
2. Start the stopclock as soon as the magnesium comes in contact with the hydrochloric acid.

Figure 17.17 Studying the rate of reaction between magnesium and excess hydrochloric acid with different concentrations of HCl.

The type of results obtained from this experiment are plotted in Figure 17.18.

- Note from the graph that the experiment with the more concentrated acid takes place more quickly than those with the less concentrated acid.
- Note also that the line of the graph for the more concentrated acid shows a steep climb upwards, i.e. a large amount of gas is coming off in a short time.
- In the experiments with the less concentrated acids, there is a less steep climb upward, i.e. the gas is coming off more slowly.
- Thus, the more concentrated the acid, the steeper the graph, i.e. the faster the rate of reaction.
- Note also that the total volume of gas given off is the same in both experiments. This is because the same mass of magnesium was used in both experiments. Since the hydrochloric acid is present in excess, it is the magnesium that determines the volume of hydrogen given off.

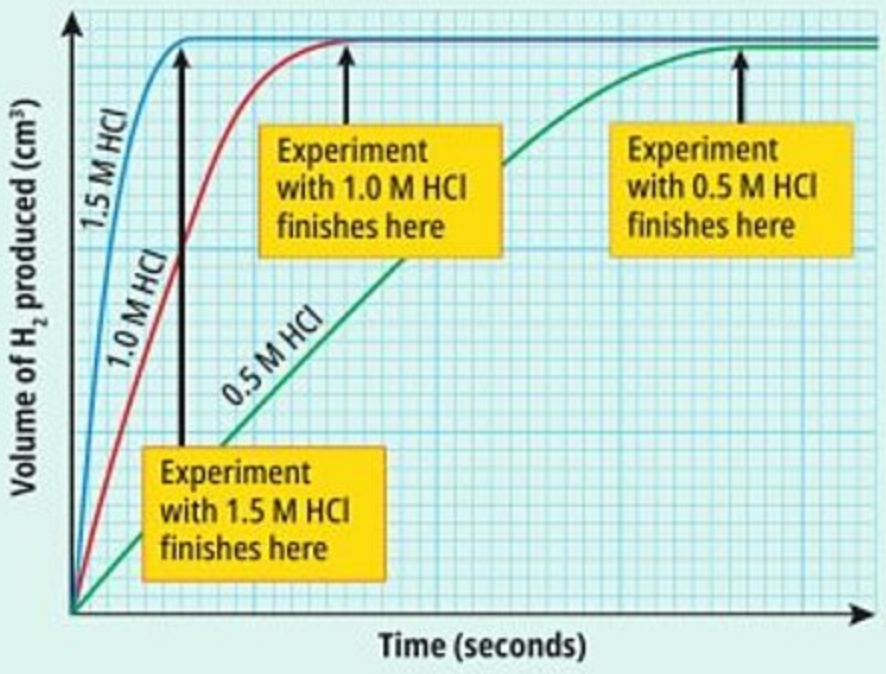

Volume of H2 produced (cm3)
1.5 M HCl
1.0 M HCl
0.5 M HCl
Experiment with 1.0 M HCl finishes here
Experiment with 0.5 M HCl finishes here
Experiment with 1.5 M HCl finishes here
Time (seconds)

Figure 17.18 The more concentrated the acid, the steeper the curve, i.e. the faster the rate. The experiment with the 1.0 M HCl is completed in a shorter time than the experiment using the 1.0 M HCl and then the 0.5 M HCl.

17.3 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 16 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 16

To study the effect of concentration on the reaction rate using sodium thiosulfate solution and hydrochloric acid

Introduction

Another experiment to study how the rate of reaction depends on concentration is the reaction between sodium thiosulfate solution and hydrochloric acid. In this experiment, we will take a number of sodium thiosulfate solutions, each having a different concentration. We will then react each of these solutions with a certain volume of dilute hydrochloric acid. The concentration and the volume of the HCl solution will be kept constant in order to have a fair test, i.e. so that only one variable (the concentration of sodium thiosulfate) is changed.

Sodium thiosulfate and hydrochloric acid react together to produce a precipitate of sulfur.

$Na_2S_2O_3 + 2HCl \rightarrow S\downarrow + 2NaCl + SO_2 + H_2O$

The sulfur does not settle but remains in suspension, giving a yellow cloudy mixture in the flask. In order to follow the rate at which sulfur is formed, we will time how long it takes for a cross drawn on a piece of paper under a flask to be obscured by the sulfur that is precipitated.

Key steps in procedure

- Using a graduated cylinder, a fixed quantity of 0.2 M sodium thiosulfate solution is poured into a conical flask.
- The conical flask is placed on a sheet of white paper on which a cross has been marked.
- Using another graduated cylinder, a fixed quantity of a hydrochloric acid solution is quickly added to the sodium thiosulfate solution in the conical flask.
- The conical flask is swirled and the stopwatch is started immediately, Figure 17.19.
- The cross is observed through the mixture.

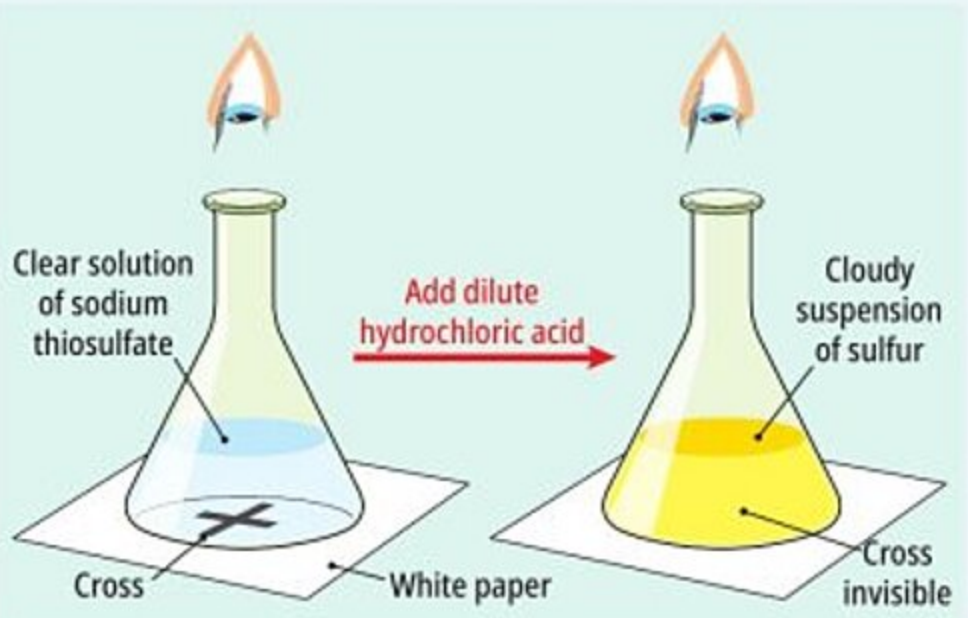


Figure 17.19 The sulfur formed by the reaction of sodium thiosulfate and hydrochloric acid obscures the cross under the conical flask.

Observation

- The mixture in the flask becomes more milky as the reaction proceeds. A creamy yellow colour is observed in the mixture in the flask.
- Eventually, it is no longer possible to see the cross through the mixture.

Explanation

- As the reaction proceeds, the sodium thiosulfate is reacting with the hydrochloric acid to form sulfur according to the equation:

  $Na_2S_2O_3 + 2HCl \rightarrow S\downarrow + 2NaCl + SO_2 + H_2O$

- Sulfur does not dissolve in water but remains in suspension in the water. This gives an appearance of 'milkiness' or a creamy yellow colour.

Procedure (continued)

- When the degree of creamy yellow precipitate of sulfur ('milkiness') reaches the stage that the cross is no longer visible, the stopwatch is immediately stopped.
- The time taken to obscure the cross is noted and this result is entered in the table.

Conc. of $Na_2S_2O_3$ (moles/L)	0.2	0.16	0.12	0.08	0.04	0.02
Time (secs)						
Rate (1/time) (sec^{-1})						

- The conical flask and the graduated cylinder that contained the sodium thiosulfate solution are rinsed out.
- The 0.2 M sodium thiosulfate solution is diluted to a concentration of 0.16 M $Na_2S_2O_3$ using deionised water.
- The experiment is repeated with the same quantity of 0.16 M $Na_2S_2O_3$ solution added to the conical flask.
- The concentration of HCl solution is kept the same and the same quantity of HCl solution is added to the conical flask.

Explanation

- The concentration of the HCl and the volume of the HCl solution are kept constant in order to ensure a fair test, i.e. so that only one variable (the concentration of the sodium thiosulfate) is changed.

Procedure (continued)

- The time taken for the cross to become obscured is noted and this result is entered in the above table.
- The experiment is repeated each time with concentrations of 0.12 M, 0.08 M, 0.04 M and 0.02 M $Na_2S_2O_3$ solutions.
- In each case the time taken for the cross to become obscured is noted.

Data Analysis 1

- A graph of time taken (y-axis) versus concentration (x-axis) is plotted. A graph similar to that shown in Figure 17.20 should be obtained.

Explanation

- The graph tells us that the cross is obscured most quickly when the solution is most concentrated.
- Another way of stating this is that, as the concentration increases, the time for the cross be obscured decreases, i.e. the rate of the reaction increases with increased concentration.

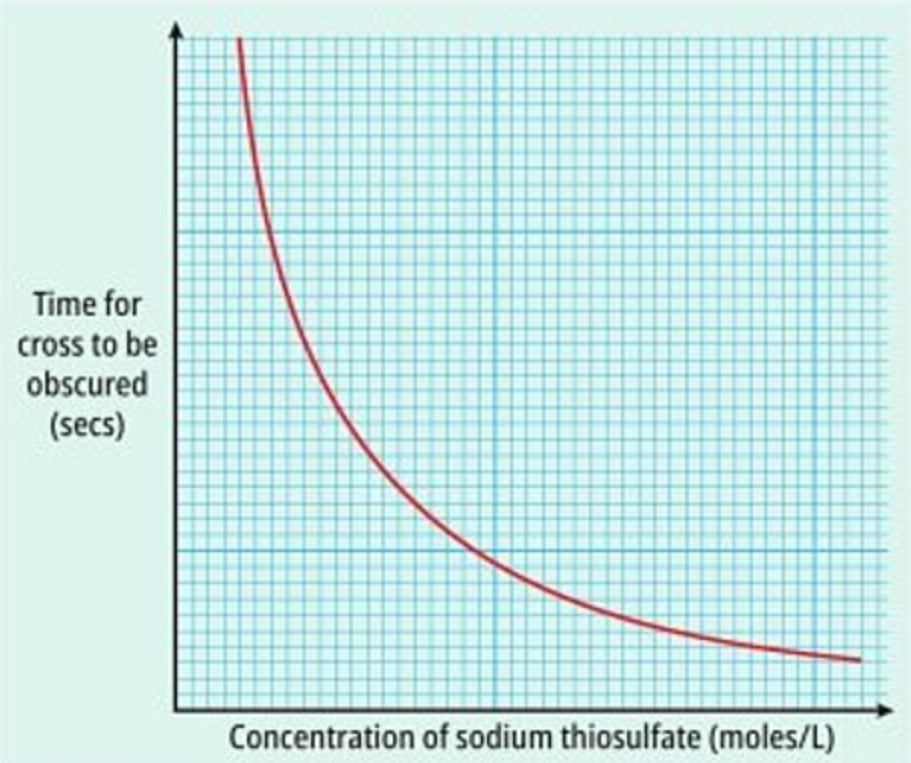


Figure 17.20 This graph shows that the more concentrated the solution of sodium thiosulfate, the less time is needed for the cross to become obscured.

Data Analysis 2

- To indicate more clearly that the rate of reaction increases with the concentration of thiosulfate ion, a graph of the rate of reaction versus the concentration of sodium thiosulfate solution could be drawn, Figure 17.21.
- Note that a straight line **through the origin** is obtained.

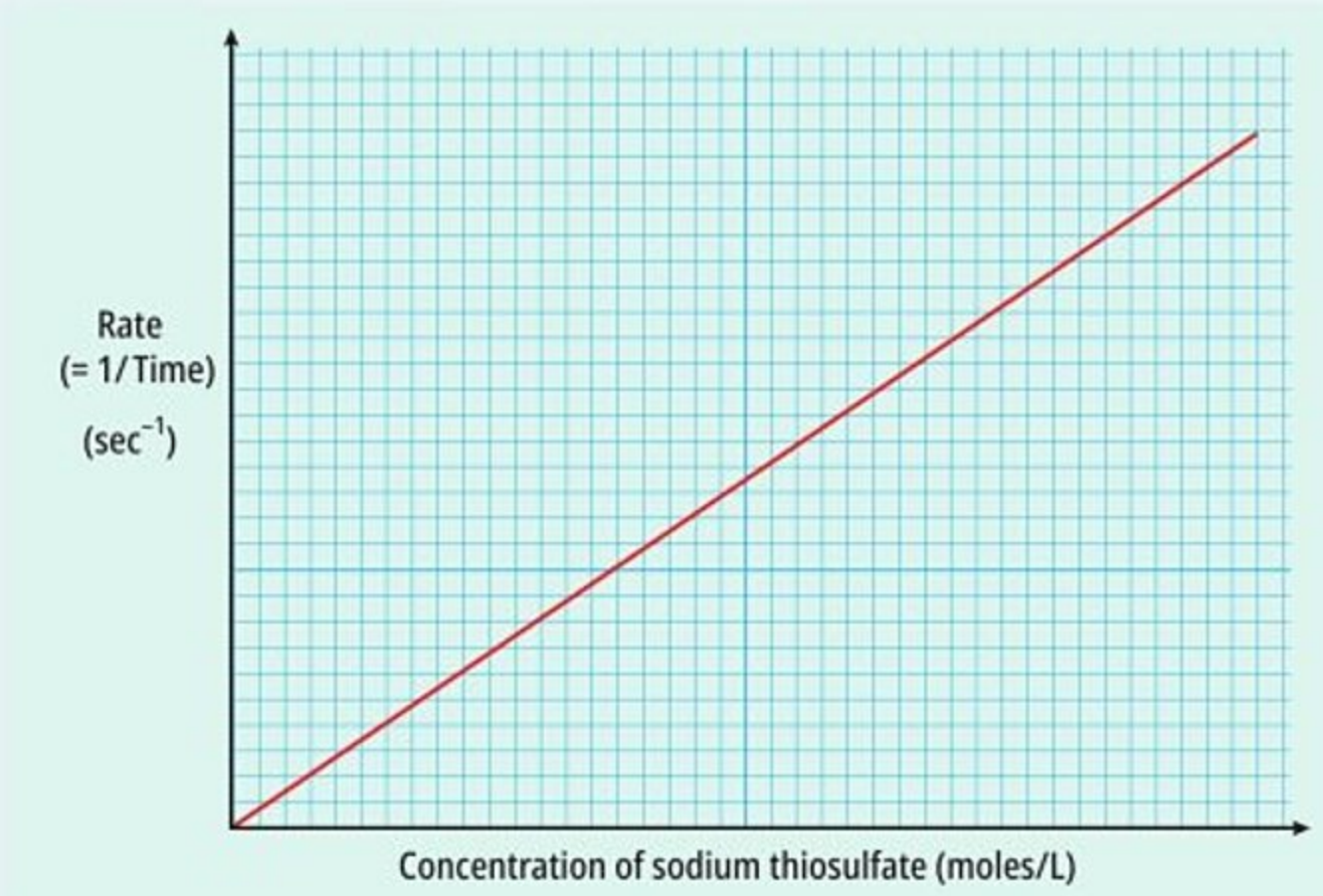


Figure 17.21 This graph shows that the rate of the reaction is directly proportional to the concentration of sodium thiosulfate solution.

Explanation

- The straight line through the origin shows that the rate of reaction is directly proportional to the concentration of the sodium thiosulfate solution.

DIGITAL: A video of this experiment is available on FolensHIVE.

In order to get an idea of the rate of a reaction, chemists often use the reciprocal of the time.

- Note that time and rate are inversely proportional.
- The shorter the time for the cross to be obscured, the faster the rate of reaction.
- For example, when the rate of reaction is doubled, the time taken for the cross to be obscured is halved.
- Conversely, the longer the length of time it takes for the cross to be obscured, the slower the rate of reaction.

To help you understand this relationship, a worked example using some data from a past Leaving Certificate Chemistry exam paper is shown in Example 17.2.

Since the rate of reaction is defined as the change in concentration per unit time of any one reactant or product:

$$\text{Rate} = \frac{\text{Change in concentration (moles/L)}}{\text{Time (secs)}}$$

$$\text{i.e. rate } \alpha \frac{1}{\text{time}}$$

Example 17.2

Question

Using the data shown in the table, plot a graph of reaction rate (1/t) versus concentration of sodium thiosulfate.

What conclusion can be drawn from the graph about the relationship between the rate of the reaction and the concentration of the sodium thiosulfate?

Concentration $Na_2S_2O_3$ (M)	0.20	0.16	0.12	0.08	0.04	0.02
Reaction time (min)	1.14	1.43	1.89	2.94	5.88	11.11
1/t (min^{-1})	0.88	0.70	0.53	0.34	0.17	0.09

[LCH]

Answer

The graph obtained is shown in Figure 17.22.

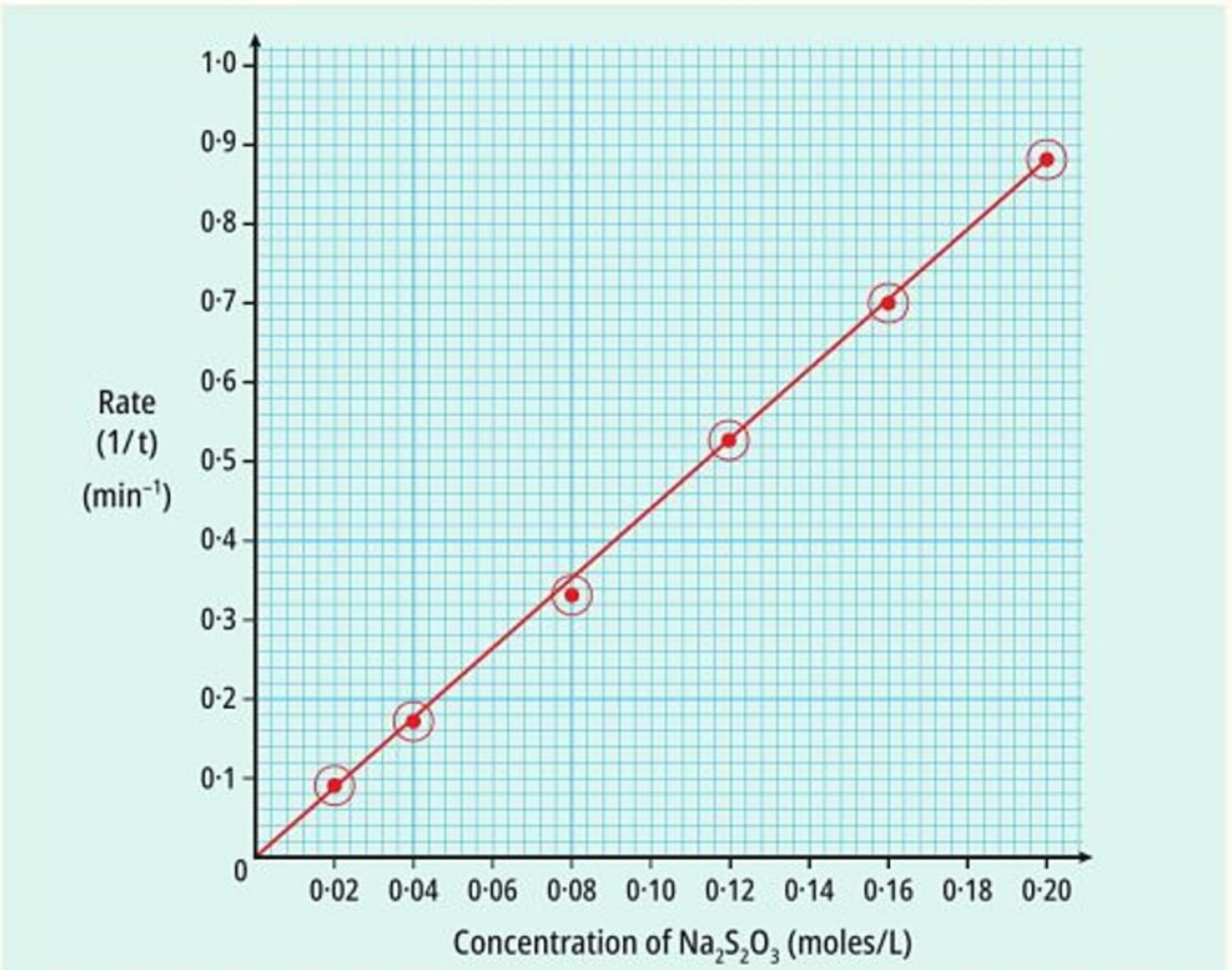


Figure 17.22 A graph of the concentration of the sodium thiosulfate solution versus the rate of reaction gives a straight line through the origin. This shows that the rate of reaction is directly proportional to the concentration of the sodium thiosulfate solution.

Conclusion

The straight line through the origin tells us that the rate of reaction is directly proportional to concentration.

(iv) Temperature

We are all aware that food keeps fresh for longer if stored in a fridge. This is because the chemical reactions that cause the food to go bad take place more slowly at the lower temperature.

To study the effect of temperature on the rate of a reaction, we use the same reaction between sodium thiosulfate and dilute hydrochloric acid as in Experiment 17.2.

17.4 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 17 in the Student Laboratory Notebook accompanying this textbook.

Student Experiment No. 17

To study the effect of temperature on reaction rate using sodium thiosulfate solution and hydrochloric acid

Introduction

In this experiment, we use the same chemical reaction studied in Experiment 17.3. However, we will use just one concentration of sodium thiosulfate solution reacting with hydrochloric acid at different temperatures. We will use quite a dilute solution of sodium thiosulfate in this experiment so that the measured times will not be too short at the higher temperatures.

Key steps in procedure

- Using a graduated cylinder, a fixed quantity of 0.05 M sodium thiosulfate is poured into a conical flask.
- The conical flask is placed on a sheet of white paper on which a cross has been made.
- Using another graduated cylinder, a fixed quantity of hydrochloric acid solution is added to the sodium thiosulfate solution in the conical flask.
- The conical flask is swirled and the stopwatch is started immediately.
- The cross is observed through the solution.
- When the degree of creamy yellow precipitate of sulfur (milkiness) reaches the stage when the cross is no longer visible, the stopwatch is immediately stopped.
- The time taken for the cross to become obscured is noted. The temperature of the solution is measured (e.g. 15 °C). The data are entered in the table.

Temperature (°C)	15	20	30	40	50	60	70
Time (secs)							
Rate (1/time) (sec^{-1})							

- The conical flask is washed out. The same quantity of sodium thiosulfate of the same concentration is added to the conical flask.
- The conical flask is heated to a higher temperature using a hot plate.
- The same quantity of hydrochloric acid of the same concentration is heated in a beaker to the same temperature as the sodium thiosulfate solution.
- The conical flask containing the thiosulfate solution is placed over the mark on the paper. The dilute hydrochloric acid is added to the conical flask and the time taken for the cross to become obscured is measured.

- The temperature of the solution in the conical flask is again measured in case some cooling has occurred.
- The experiment is repeated for a range of temperatures of around 30 °C, 40 °C, 50 °C, 60 °C and 70 °C, Figure 17.23.

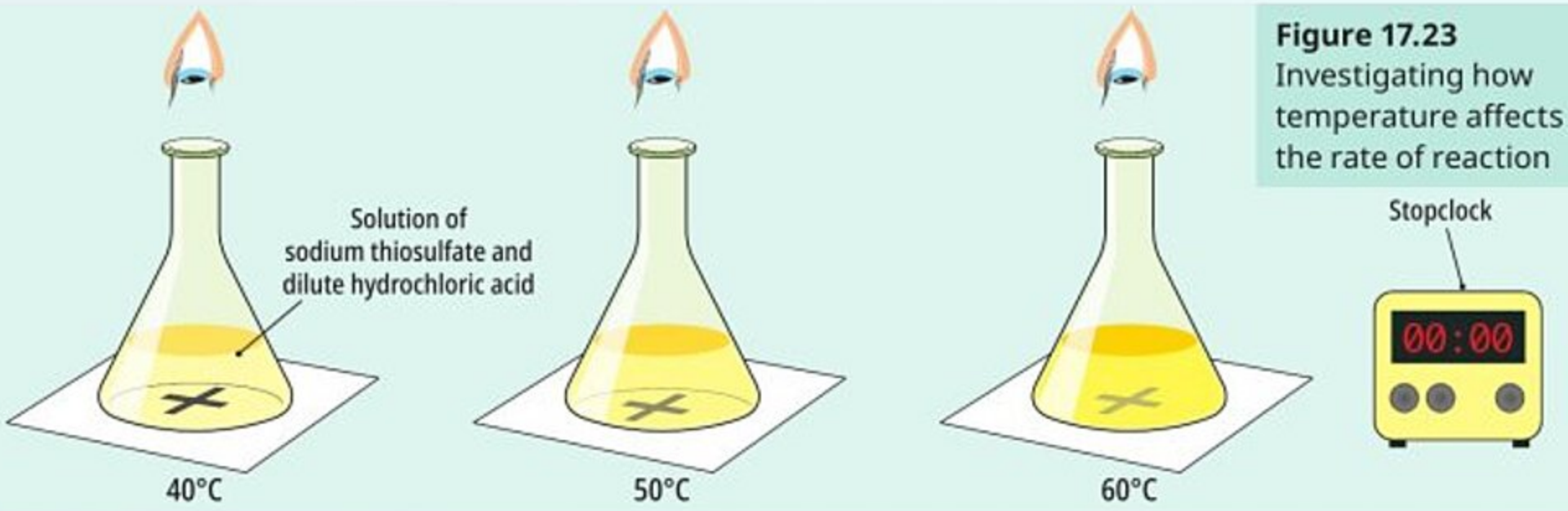


Figure 17.23 Investigating how temperature affects the rate of reaction

Data Analysis 1

- The results of the experiments can be represented by plotting the time taken against the temperature, Figure 17.24.
- It is clear from Figure 17.24 that the hotter solution takes less time to obscure the cross, i.e. the reaction times decrease with increasing temperature because increased temperature causes an increased reaction rate.

Data Analysis 2

- The results of the experiment can also be represented by plotting the reciprocal of the time (i.e. the rate) against the temperature, Figure 17.25.
- This graph shows clearly that the rate of the reaction increases with temperature. Note that the rate of reaction is **not** directly proportional to the temperature, since we do not get a straight line passing through the origin.

Chemists have discovered that, for many reactions, the rate of the reaction is approximately doubled for every 10 °C rise in temperature. We will see at a later stage that, because a rise in temperature causes the rate of a reaction to increase, many industrial processes are carried out at high temperatures.

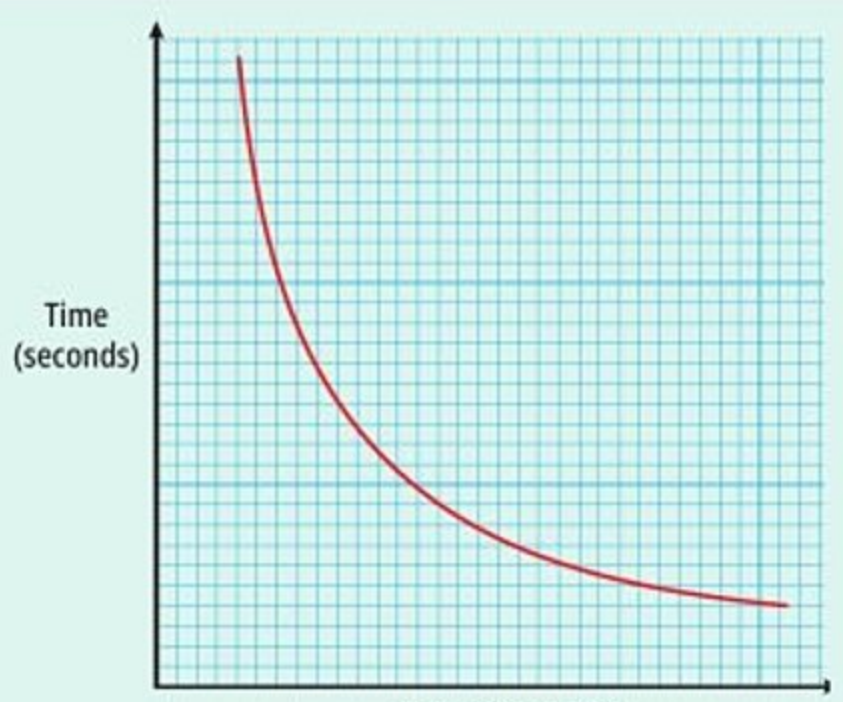


Figure 17.24 The higher the temperature, the less time it takes for the cross to be obscured.

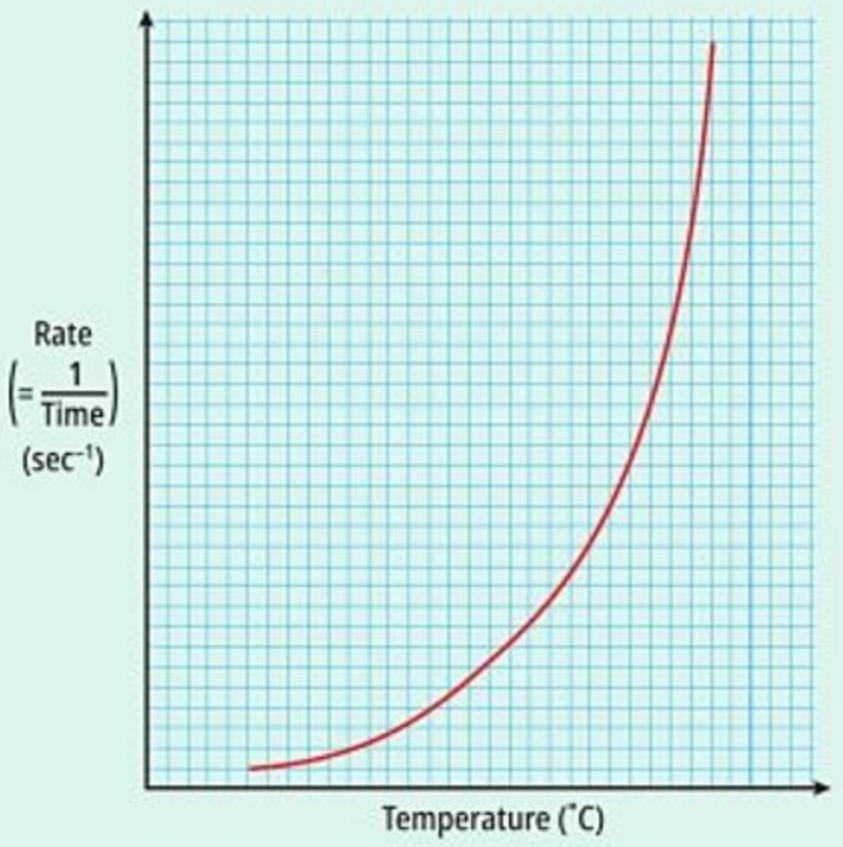


Figure 17.25 An increase in temperature causes an increase in the rate of the reaction.

DIGITAL: A video of this experiment is available on FolensHIVE.

TEST YOURSELF: Test Yourself: Attempt Questions 17.1 and W17.1–W17.2.

(v) Catalysts

We have already seen in Experiment 17.1 that a substance called manganese dioxide, when added to hydrogen peroxide, helps the hydrogen peroxide to decompose more rapidly.

$$H_2O_2 \xrightarrow{MnO_2} H_2O + \tfrac{1}{2}O_2$$

If you were to measure the mass of manganese dioxide present at the beginning of the experiment, you would find that the same mass of manganese dioxide would be present at the end of the experiment, i.e. the manganese dioxide is not used up in the reaction. We say that the manganese dioxide is a **catalyst**.

A **catalyst** is a substance that alters the rate of a chemical reaction but is not consumed in the reaction.

- Note that the definition uses the word 'alters' rather than 'speeds up'.
- This is because, while most catalysts are used to speed up reactions, some can be used to slow reactions down.
- Those catalysts that have a retarding effect are called **negative catalysts** or **inhibitors**. Glycerine is an example of a negative catalyst. It is sometimes added to hydrogen peroxide to slow down its rate of decomposition when it is being stored.

We will now study catalysts under the following headings:

(a) General properties of catalysts
(b) Types of catalysis
(c) Mechanisms of catalysis

(a) General properties of catalysts

The general properties of catalysts may be summarised as follows:

- Catalysts play an active part in chemical reactions and are recovered **chemically unchanged** at the end of a reaction. For example, if the manganese dioxide used to catalyse the decomposition of hydrogen peroxide is examined before and after the decomposition reaction has taken place, it is found to have exactly the same chemical properties.
- Catalysts tend to be **specific**, i.e. a catalyst catalyses one particular reaction or sometimes a class of very similar reactions, e.g. platinum catalyses many hydrogenation (addition of hydrogen) reactions. However, other broadly similar reactions may not be catalysed, e.g. platinum may not catalyse other addition reactions. Biological catalysts called enzymes, which are produced by living cells, tend to be extremely specific.

For example, liver contains an enzyme called *catalase*. This enzyme decomposes hydrogen peroxide in living things. Hydrogen peroxide is highly toxic to living cells and is constantly being produced as a result of chemical reactions in the cells. It is essential that hydrogen peroxide be decomposed as soon as it is formed.

An **enzyme** is a substance that is produced by a living cell and acts as a biological catalyst.

The enzyme catalase acts so quickly to break down the hydrogen peroxide that it is the fastest enzyme known. The effect of the enzyme catalase on hydrogen peroxide is shown in Figure 17.26.

- Large amounts of enzymes are used in the manufacture of biological washing powders.
- These washing powders contain enzymes that catalyse the breaking down of the chemicals in food and other stains on clothing. Almost all of the enzymes in washing powders are *hydrolases* – enzymes that catalyse the breaking down (hydrolysis) of fats, proteins and carbohydrates.
- An enzyme called *protease* is used in washing powders for its ability to digest protein-based stains, such as blood, at low temperatures.

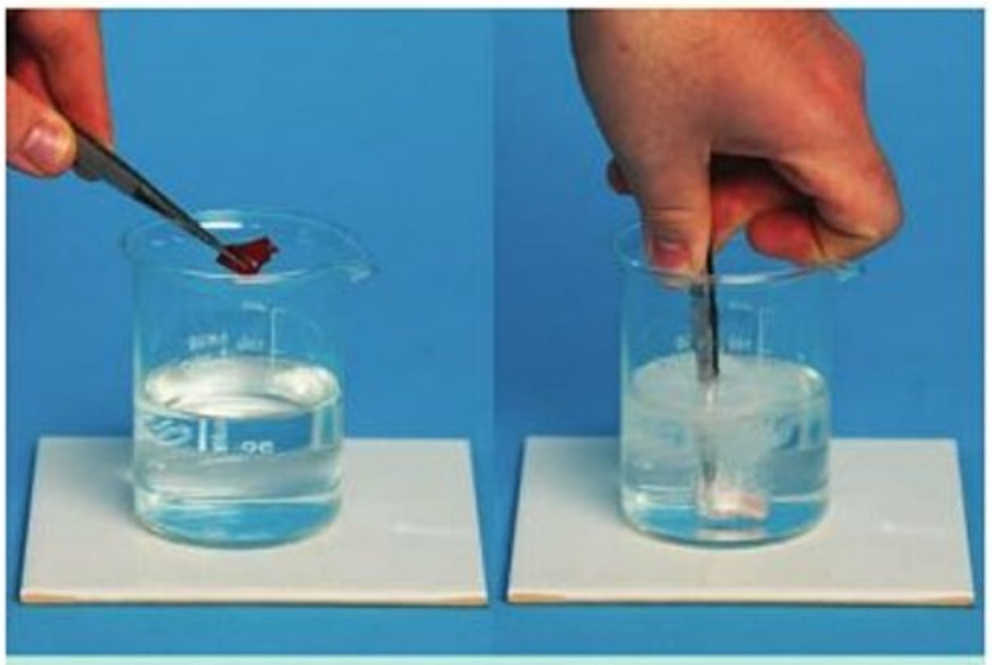


Figure 17.26 Liver contains an enzyme called catalase which acts as a catalyst in the decomposition of hydrogen peroxide.

Catalysts need only be present in very **small amounts** to function as catalysts. You may assume that in the reactions studied in this course, increasing the amount of catalyst does not significantly alter the rate of the reaction. The effect on the rate of altering the amount of catalyst varies depending on the reaction itself. The effect can only be determined by experiment.

- In the case of **equilibrium reactions**, a catalyst helps equilibrium to be achieved more quickly. However, it does not affect the position of equilibrium or the composition of the final mixture in an equilibrium reaction. This will be studied in more detail in Chapter 18.
- The action of a catalyst may be destroyed by certain substances called **catalyst poisons**, e.g. in the past when lead was added to petrol, it was found that the lead destroyed the catalysts in the catalytic converters in cars. Another example of a catalyst poison is arsenic. This is very dangerous because it inhibits the actions of certain enzymes in the body.

Some of the general properties of catalysts are summarised in Figure 17.27.

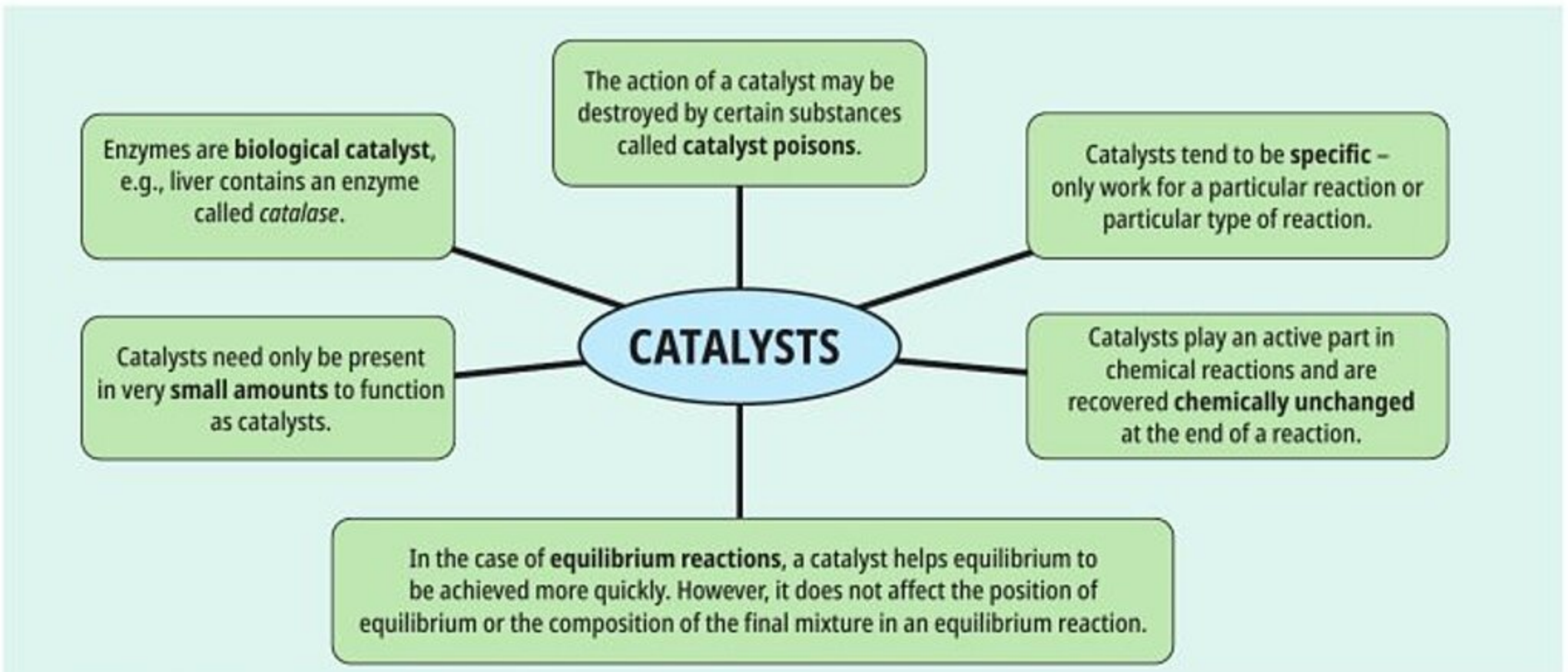

CATALYSTS
Enzymes are biological catalyst, e.g., liver contains an enzyme called catalase.
The action of a catalyst may be destroyed by certain substances called catalyst poisons.
Catalysts tend to be specific – only work for a particular reaction or particular type of reaction.
Catalysts need only be present in very small amounts to function as catalysts.
Catalysts play an active part in chemical reactions and are recovered chemically unchanged at the end of a reaction.
In the case of equilibrium reactions, a catalyst helps equilibrium to be achieved more quickly. However, it does not affect the position of equilibrium or the composition of the final mixture in an equilibrium reaction.

Figure 17.27 Some general properties of catalysts

(b) Types of catalysis

Chemists have discovered that there are three types of catalysis – homogeneous catalysis, heterogeneous catalysis and autocatalysis.

(i) Homogeneous Catalysis

Homogeneous catalysis means catalysis in which both the reactants and the catalyst are in the same phase, i.e. there is no boundary between the reactants and the catalyst.

- Note the use of the word 'phase' in this definition. A phase is a specific state of matter that has uniform chemical and physical properties. For example, if you mix oil and water, they form two phases (an oil phase and a water phase). Even though both oil and water are in the same state of matter (liquid), they are in different phases because there is a boundary between them.

Figure 17.28 The iodine snake is an example of homogeneous catalysis!

- An example of homogeneous catalysis is the 'iodine snake' experiment. In this experiment, some concentrated potassium iodide solution (the catalyst) is added to washing-up liquid and some hydrogen peroxide solution is then added. Potassium iodide catalyses the decomposition of hydrogen peroxide into water and oxygen. Both liquids are in the same phase, i.e. there is no boundary between them. The oxygen is quickly released and gets trapped in the washing-up liquid. Foam is produced and is carried out of the bottle in the form of a snake as shown in Figure 17.28.

(ii) Heterogeneous Catalysis

- An example of this type of catalysis is the decomposition of hydrogen peroxide (liquid) catalysed by manganese dioxide (solid). In this case there is a physical solid-liquid boundary between the manganese dioxide and the hydrogen peroxide, i.e. manganese dioxide does not dissolve in the hydrogen peroxide.
- Another example is the catalytic oxidation of methanol (liquid) by platinum (solid). The following is the reaction that occurs:

Heterogeneous catalysis is catalysis in which the reactants and the catalyst are in different phases, i.e. there is a boundary between the reactants and the catalyst.

$$2CH_3OH + O_2 \xrightarrow{Pt} 2HCHO + 2H_2O$$

Methan**ol** → methan**al**

Note the almost identical spelling of the two chemicals. Methanol is one of a family of chemicals called alcohols. Methanal is one of a family of chemicals called aldehydes. We will be studying these chemicals in more detail in Chapter 24. The experiment to demonstrate the oxidation of methanol to methanal is shown in Figure 17.29.

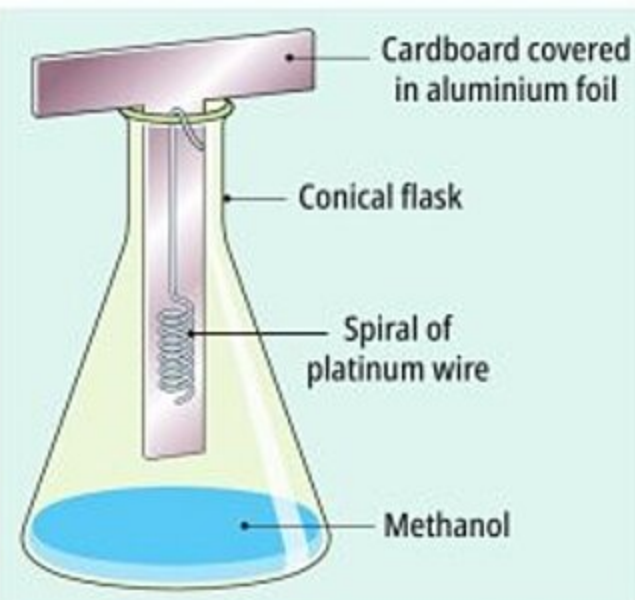


Figure 17.29 Methanol is oxidised to methanal using platinum as a catalyst. This is an example of heterogeneous catalysis.

The main points about this experiment may be summarised as follows:

Key steps in procedure

- About 25 cm^3 of methanol are placed in a 250 cm^3 conical flask. A piece of cardboard in the shape of a T-piece and covered with aluminium foil is suspended in the conical flask. The purpose of the aluminium foil is to prevent the cardboard catching fire.
- In the fume cupboard, the methanol is warmed to about 60 °C and placed on a heat-resistant mat to keep it warm.
- A spiral of platinum wire (the catalyst) is held by a tongs and heated until it is red hot using a Bunsen burner.
- The hot spiral of platinum wire is quickly hung inside the conical flask.

Observation

- The hot spiral, which will have cooled during the transfer, will begin to glow red hot again.
- There will be a number of mild 'pops' or mini explosions.
- A repeating cycle of occurrences takes place, i.e. the spiral glows, then there is a mini-explosion, the spiral cools down, then the spiral heats up again, then there is another mini-explosion, and so on.
- The smell of methanal may be noticed. Avoid smelling it directly as it is poisonous and produces tears.
- A flame may be observed in the flask.

Explanation

- The T-piece acts as a chimney to allow waste gases to be swept away and more air to flow into the conical flask.
- The T-piece is covered in aluminium foil to prevent the cardboard being burned.
- The platinum glows because the reaction taking place is exothermic, i.e. it gives out heat.
- The glowing ceases for a while because carbon monoxide is formed due to incomplete combustion of the methanol. This carbon monoxide poisons the catalyst. Once the carbon monoxide leaves the platinum, the platinum again works as a catalyst and the glowing starts again.
- The flame inside the flask is caused by the hot wire igniting the methanol vapour. The flame is extinguished when the oxygen in the air inside the flask is used up.

The popping sounds are caused by hydrogen exploding. In the absence of sufficient oxygen, methanol is oxidised (catalytic dehydrogenation) to methanal and hydrogen gas:

$$CH_3OH \rightarrow HCHO + H_2$$

A photograph of the reaction taking place is shown in Figure 17.30.

Figure 17.30 When methanol is oxidised to methanal, the heat given out in the exothermic reaction causes the platinum wire to glow.

(iii) Autocatalysis

You may recall that we studied the reaction between permanganate ions and iron(II) ions in Chapter 15.

$$MnO_4^- + 8H^+ + 5Fe^{2+} \rightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

In performing this titration, you may have observed that the first few drops of potassium permanganate were decolorised slowly but subsequent drops were decolorised more rapidly. This is because the reaction is catalysed by the Mn^{2+} ions formed in the reaction. The type of catalysis where one of the products of the reaction catalyses the reaction itself is called **autocatalysis.**

Autocatalysis is catalysis in which one of the products of the reaction acts as a catalyst for the reaction.

- An autocatalytic reaction starts slowly but speeds up as the catalyst product starts to form.

(c) Mechanisms of catalysis

Knowledge of catalysis is very important for chemists, as it helps them to speed up or slow down chemical processes in industry. A lot of research takes place into obtaining a clear picture of the mechanisms of catalysis, i.e. how catalysts work. It has been discovered that there are two general mechanisms which explain how catalysts work.

1. The intermediate formation theory

This theory may be summarised as follows:

- Arrhenius suggested that a catalyst works by forming an intermediate compound. Consider the general reaction:

$$W + X \rightarrow Y + Z$$

Arrhenius suggested that one (or sometimes more than one) of the reactants combines with the catalyst to form an intermediate compound. This intermediate compound may only exist for a very short time and may be difficult to detect.

$$\underset{\text{reactant}}{W} + \underset{\text{catalyst}}{C} \rightarrow \underset{\text{intermediate}}{[WC]}$$

- This intermediate then reacts with the other reactant to give the final product and regenerate the catalyst.

$$[WC] + X \rightarrow Y + Z + \underset{\text{catalyst}}{C}$$

Overall reaction: $W + X \rightarrow Y + Z$

- The decomposition of hydrogen peroxide catalysed by the presence of I^- ions ('iodine snake' reaction) illustrates the formation of the intermediate.

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2$$

Step 1

One of the hydrogen peroxide molecules reacts with an I^- ion to form the IO^- intermediate, Figure 17.31.

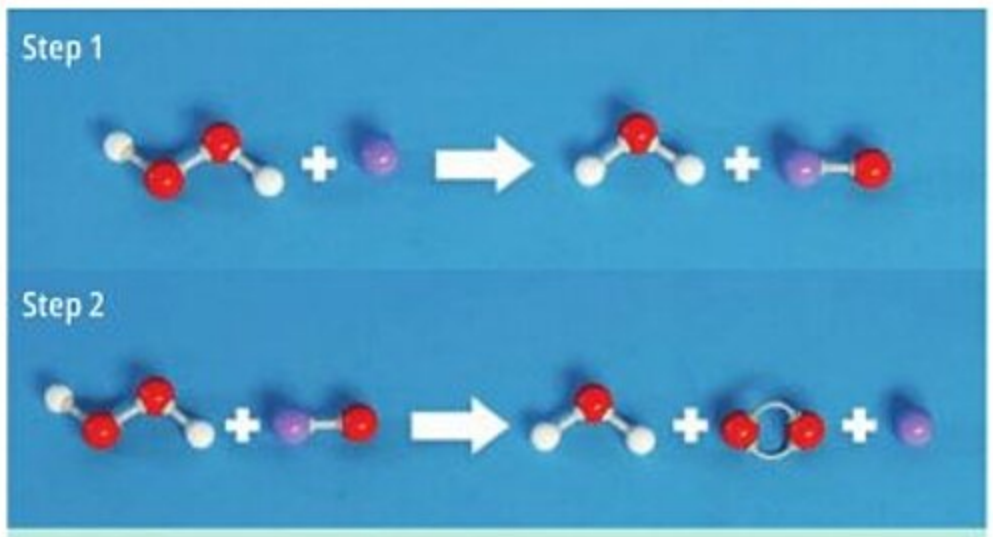


Figure 17.31 The IO^- ion is the intermediate formed when I^- ions are used to catalyse the decomposition of hydrogen peroxide.

$$H_2O_2 + I^- \rightarrow H_2O + \underset{\text{intermediate}}{IO^-}$$

Step 2

The intermediate then reacts with another hydrogen peroxide molecule to form the products and regenerate the catalyst.

$$H_2O_2 + IO^- \rightarrow H_2O + O_2 + I^-$$

Adding the equations in Steps 1 and 2 gives us the overall equation:

$$2H_2O_2 \xrightarrow{I^-} 2H_2O + O_2$$

Evidence for the Intermediate Formation Theory of Catalysis

An experiment that provides visual evidence for the Intermediate Formation Theory is the oxidation of a compound called potassium sodium tartrate (don't worry about the formula!) using hydrogen peroxide.

- This reaction is catalysed by the presence of Co^{2+} ions, which have a pink colour.
- Some potassium sodium tartrate is dissolved in hot water and some crystals of pink cobalt(II) chloride (the catalyst) are added.
- The beaker is placed on a tripod standing in a dish, Figure 17.32.

Figure 17.32 (a) The hydrogen peroxide is about to be added to the potassium sodium tartrate. The pink colour is due to the presence of Co^{2+} ions.

(b) The green colour is evidence for the existence of an intermediate compound.

(c) The pink colour is restored again, indicating that the Co^{2+} ions have not been used up but have been reformed again at the end of the experiment.

Observation

- The solution is pink at the start of the experiment due to the presence of Co^{2}+ ions.
- After adding some 100-volume hydrogen peroxide, fizzing is observed.
- The solution changes to a green colour.
- After a short while, the fizzing stops and the green colour changes back to a pink colour again.

Explanation

- The colour change from pink to green indicates the formation of a new substance, i.e. the green colour is the colour of the new substance.
- The change of the green colour of the new substance back to the original pink colour suggests that the new substance is an intermediate.
- The fizzing of the solution while it is green suggests that the intermediate is reacting. (The fizzing is caused by carbon dioxide being given off.)
- The fact that the pink colour is restored at the end suggests that the Co^{2+} ions have not been used up but are reformed at the end of the reaction, i.e. the catalyst has been regenerated.

2. The Surface Adsorption Theory

Although some examples of heterogeneous catalysis may be explained in terms of the Intermediate Formation Theory, most heterogeneous catalysis reactions are explained using a theory called the **Surface Adsorption Theory**.

- We must be careful to distinguish between the words 'adsorption' and 'absorption'.
- We are familiar with the word 'absorption' to describe what happens when one substance moves into another, e.g. a sponge absorbing water.
- However, the word 'adsorption' refers to the accumulation of substances only at the surface of another substance, e.g. gas molecules accumulating on the surface of a solid.
- A good example of adsorption is in the reaction between hydrogen and oxygen to form water in the presence of a platinum catalyst. At room temperature the two gases, hydrogen and oxygen, do not react. However, if we add some finely divided platinum to the mixture, it is found that the reaction proceeds rapidly.

$$2H_{2(g)} + O_{2(g)} \xrightarrow{\text{Platinum}} 2H_2O_{(g)}$$

There are three main steps involved in the mechanism of this reaction.

1. Adsorption stage

- Hydrogen and oxygen molecules diffuse towards the surface and settle on (are adsorbed on) the surface of the pieces of platinum.
- The oxygen and hydrogen molecules are held on the surface of the platinum by temporary bonds formed between these molecules and the platinum, Figure 17.33.
- Since platinum is a transition metal, it has vacant d orbitals that help the molecules to form temporary bonds with it, i.e. the molecules are chemically attached to (chemisorbed on) the platinum.

2. Reaction on surface

- Since the oxygen and hydrogen molecules are adsorbed on the surface, the higher concentration of these molecules on the surface of the catalyst makes it more likely that the molecules will collide with each other.
- This will result in bonds being broken and new bonds being formed, i.e. a chemical reaction will occur to form water molecules on the surface of the platinum.
- The reaction is helped by the fact that the covalent bonds holding the atoms together are weakened by the formation of new bonds between the reactants and the surface of the catalyst.

3. Desorption stage

- The final stage (called the **desorption stage**) is when the products leave the surface of the catalyst. In this case, the gaseous water molecules leave the surface of the catalyst and diffuse away from the catalyst.
- More reactants are then adsorbed on to the surface of the catalyst and the whole process repeats over and over again.
- It is found that the more finely divided the catalyst, the better is its performance. This is because there is a greater surface area on which adsorption can take place.

Note: The specific locations on the surface of the catalyst where the above steps take place are called the **active sites** of the catalyst.

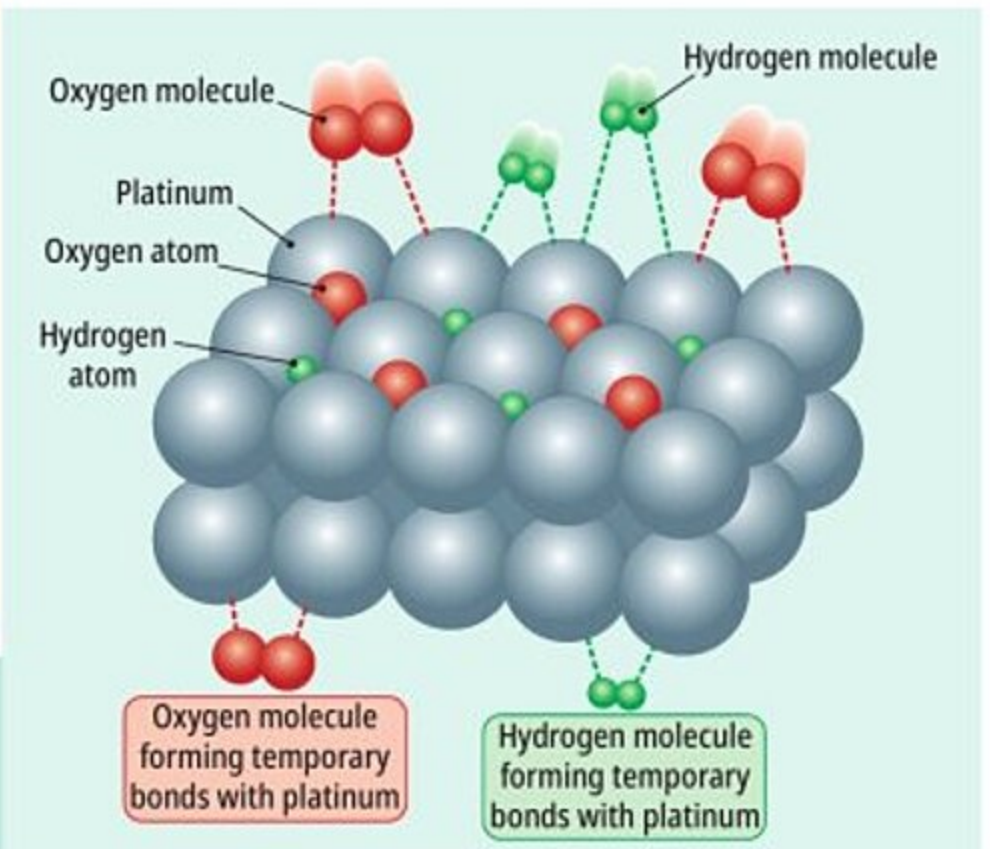


Figure 17.33 Hydrogen and oxygen molecules are adsorbed on to the surface of the platinum. The adsorbed molecules form weak bonds with the metal atoms.

Poisoning of catalysts

Catalysts may not affect the rate of a reaction if they are made ineffective. As an example of this problem, let's study the catalysts that exist in vehicles with internal combustion engines. The exhaust fumes from vehicles which burn fuels such as petrol and diesel in the internal combustion engine are a major source of air pollution. These exhaust fumes contain carbon monoxide, CO, nitrogen monoxide, NO, nitrogen dioxide, NO_2 and unburned hydrocarbons (i.e. compounds containing only carbon and hydrogen).

The sources of these fumes may be summarised as follows:

- The carbon monoxide comes from the incomplete combustion of hydrocarbons in the fuel.
- The oxides of nitrogen in the exhaust fumes are commonly referred to as NO_x compounds. These oxides of nitrogen are formed because, when any fuel is burned in air at high temperatures, some of the nitrogen gas in the air is oxidised to form nitrogen monoxide, NO, which reacts with more oxygen to form nitrogen dioxide, NO_2.
- In former times, when leaded petrol was used as a fuel, lead compounds were also emitted in the exhaust fumes.
- The unburned hydrocarbons arise from the fact that some of the fuel is not burned in the engine and the hydrocarbons are emitted in the exhaust fumes.
- It is very important to reduce the above emissions as much as possible. Carbon monoxide is a colourless, odourless and tasteless gas that is highly poisonous. The oxides of nitrogen, as well as being poisonous, also contribute to acid rain. The unburned hydrocarbons can give rise to smog.
- One method of converting these environmentally harmful gases into harmless gases is to place a catalytic converter into the exhaust system of a motor vehicle.

Looking at the catalytic converter from the outside, it appears just like an extra silencer box on the car's exhaust system, Figure 17.34.

A catalytic converter consists of a thin coating of the metals **platinum**, **palladium** and **rhodium** (the catalysts) on a ceramic or metal 'honeycomb' inside a stainless steel case, Figure 17.35. The catalysts are spread over the surface of the honeycomb, which has a huge surface area – as large as two or three football fields! The mixture of hot harmful gases (at a temperature of around 300 °C) is then converted into much less harmful products.

A **catalytic converter** is a device in the exhaust system of a motor vehicle which contains catalysts to convert pollutants in the exhaust gases to less harmful substances.

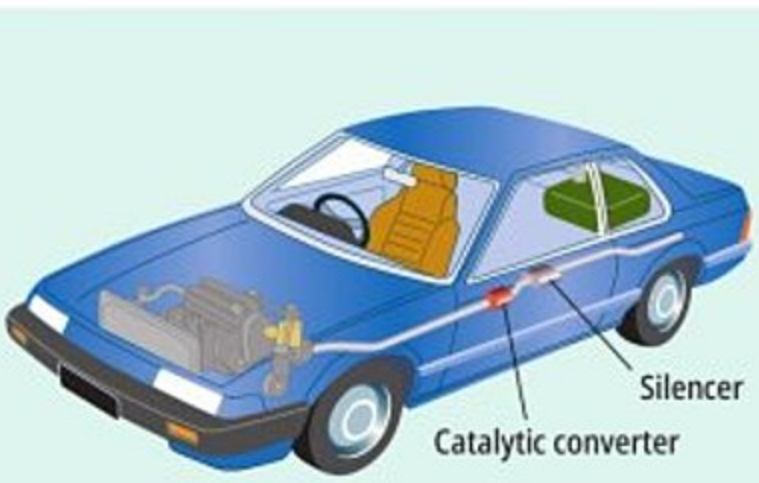


Figure 17.34 A catalytic converter is fitted into the exhaust system of cars powered by fossil fuels to convert the harmful gases into less harmful ones.

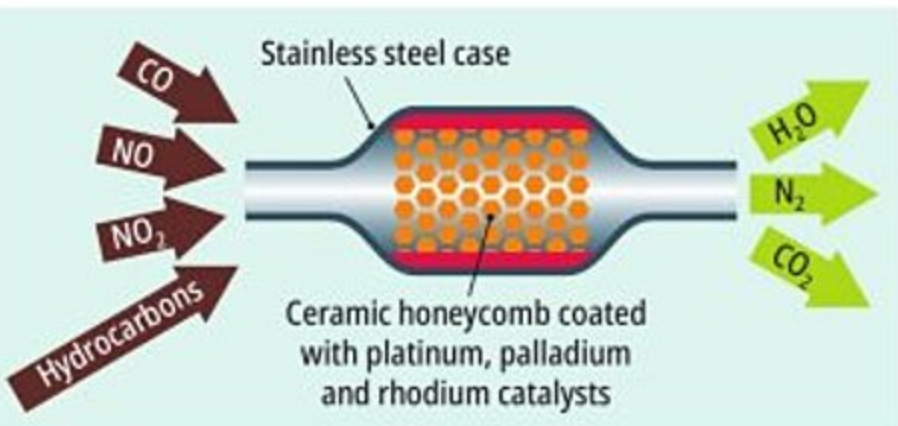


Figure 17.35 The main gases entering a catalytic converter and leaving a catalytic converter

The main reaction that happens in the catalytic converter is the reaction between the polluting gases themselves (carbon monoxide and nitrogen monoxide) to form carbon dioxide and nitrogen:

$$2CO + 2NO \xrightarrow{Pt/Pd/Rh} 2CO_2 + N_2$$

Also, the unburned hydrocarbons react with the nitrogen oxides to form carbon dioxide and nitrogen and water. Note that the pollutants are being converted to CO_2, N_2 and H_2O, all of which are naturally present in the air. The environmental benefits of catalytic converters may be summarised in the form of a table.

Reactant	Product	Environmental benefit of removal
Carbon monoxide	Carbon dioxide	Carbon monoxide is a poisonous gas.
Nitrogen monoxide	Nitrogen	Nitrogen monoxide is poisonous and contributes to acid rain.
Hydrocarbons	Carbon dioxide and water	Hydrocarbons cause smog and contribute to the greenhouse effect.

Note also that the chemical equation describing what takes place in a catalytic converter is a good example of heterogeneous catalysis, since the reactants and the catalysts are in different phases.

Catalytic converters usually last for about 80,000 kilometres. They need to be replaced as a result of 'poisoning' of the catalyst and disintegration of the catalysts and the ceramic surfaces as a result of engine vibration and wear from fast-moving hot gases. However, when leaded petrol was used as a fuel, the catalytic converter had a very short life. It was ruined as the lead poisoned the surface of the catalysts.

- When a catalyst is 'poisoned', a lot of the surface of the catalyst is blocked off due to permanent bond formation between the metal and the substance acting as the catalyst poison.
- Catalytic poisoning takes place when substances chemically bind to the catalyst's surface. These block the active sites on the catalyst that help to break down the harmful exhaust gases.

A **catalyst poison** is a substance that makes a catalyst inactive.

The lead compounds are more strongly adsorbed on to the surface of the catalyst than the other compounds and thus 'poison the catalyst' or prevent the catalyst from doing its job. A lot of the surface of the catalyst is blocked off due to permanent bond formation between the catalyst and the substance acting as the catalyst poison. Although lead is no longer added to petrol, catalysts in catalytic converters can still be poisoned by other substances:

- Sulfur compounds: These compounds found in fuels or oil can coat the surface of the catalyst. Modern fuels usually have low amounts of sulfur but contamination can still occur.
- Phosphorus: If the engine burns oil, phosphorus compounds can enter the exhaust system and poison the catalyst.
- Plastic silicone compounds: These are used for sealants and, when burned, the silicon deposits can poison the catalyst.

When the converter is changed, it is possible to recover most of the catalysts and recycle them. Each catalytic converter contains only a few grams of the catalysts, Figure 17.36.

Figure 17.36. This photograph shows the ceramic honeycombs used in catalytic converters.

Note: Catalysts can also become **saturated** when the active sites on the catalyst are temporarily occupied by reactants or intermediates. Since the catalysts are now working at full capacity, the effectiveness of the catalysts is reduced as they are unable to deal efficiently with the high concentration of gases. Once the reactants are converted to products and are desorbed from the surface of the catalyst, the actives sites are freed up again.

Active sites may be compared to seats in a cinema. Each seat can accommodate a person (reactant molecule). If all seats are occupied, people have to wait until one becomes available. If someone spills ice cream on a seat (poisoning), that seat becomes unavailable to accommodate new arrivals.

(vi) Pressure (for gaseous reactions)

For reactions in which all the reactants and products are gases, when you increase the pressure of the gaseous reactants, you compress the gas particles into a smaller volume. Therefore, the gas particles are closer together and they collide more frequently with each other. Since the particles collide more frequently with each other, there is a higher chance that more collisions will form products. Therefore, the reaction rate increases.

In general, for all-gaseous reactions, an increase in pressure results in an increase in reaction rate. We will be studying reactions between gases in more detail in the next chapter.

17.5 Collision theory and activation energy

Many of the observed facts about rates of reactions are interpreted using a theory called the **Collision Theory.** This theory was developed from the kinetic theory of gases in order to account for the factors that influence the rate of a reaction.

The basic assumptions of this theory are:

1. For a reaction to occur, the reacting particles must collide with each other.
2. A collision only results in the formation of products if a certain minimum energy is exceeded in the collision. Such a collision is called an **effective collision**.

An **effective collision** is one that results in the formation of products.

- For an effective collision to take place, the particles must have sufficient energy (must be moving quickly) and must collide head on. If the collision is at the wrong angle, the particle may just glance against each other and no reaction will occur. In short, collisions need to be oriented correctly, Figure 17.37. Note that an ineffective collision and an effective collision are shown in Figure 17.37. In the effective collision, an O atom is formed. This oxygen atom can then collide with other O atoms to form an oxygen molecule.

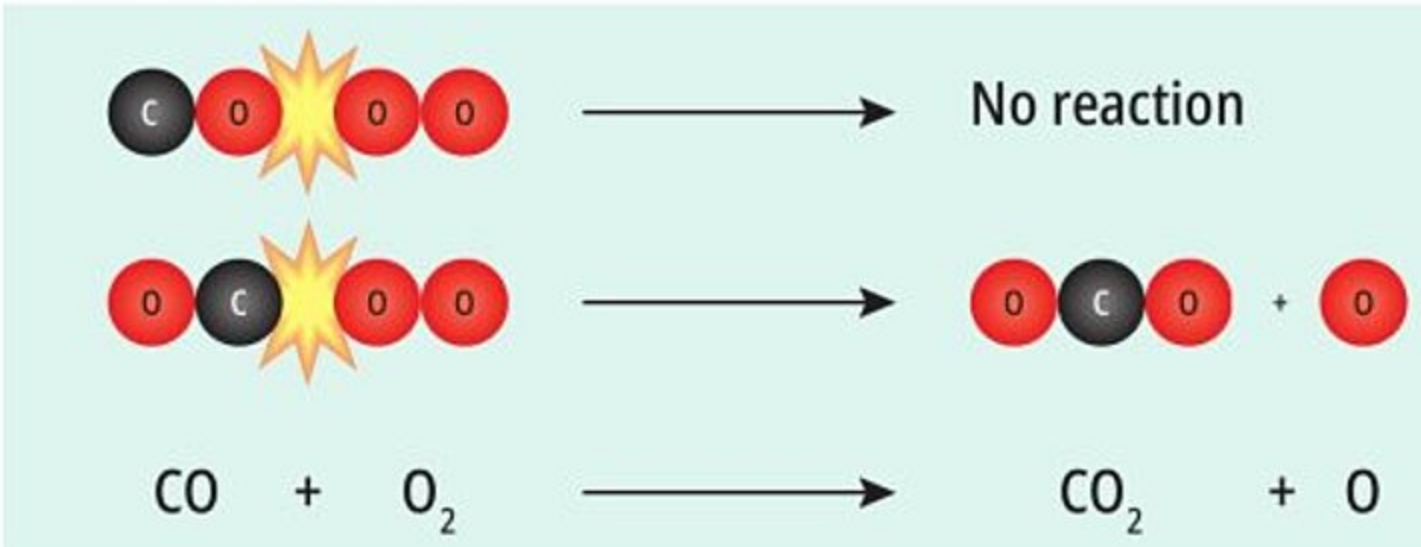


Figure 17.37 When molecules collide in the right orientation, there is a higher chance that bonds will break, and products will be formed.

- When an effective collision occurs between colliding particles, bonds are broken and new bonds are formed, i.e. the effective collision brings about a chemical reaction.
- This results in the formation of products. According to the collision theory, the rate of a reaction depends not only on the number of collisions per second that take place between the reacting particles, but also on the fraction of these collisions that are effective.

Suppose that one mole of oxygen gas and one mole of hydrogen gas are placed in a one litre container at room temperature and at a pressure of one atmosphere. It has been calculated that 1×10^{30} collisions take place every second between the molecules. If every one of these collisions were to lead to chemical reaction, the reaction would be over in a fraction of a second. However, by experiment, this is found not to be the case.

Chemists conclude that it is not the total number of collisions that will determine the rate of reaction but rather the number of **effective** collisions.

Suppose you were to measure the walking speeds of people in the street. You would find that some are walking very slowly, some are walking very quickly, and the majority are walking at moderate speeds. Similarly, if you were to calculate the amount of energy possessed by the molecules in a sample of gas, you would find that most of the molecules have an average kinetic energy, some have a lower than average kinetic energy and some have a higher than average kinetic energy. This distribution of kinetic energies of the molecules of a gas at 15 °C is shown in Figure 17.38. This type of graph is called the **Maxwell–Boltzmann distribution**. James Maxwell and Ludwig Boltzmann calculated the proportion of molecules with a given energy at a particular temperature. They drew diagrams similar to that shown in Figure 17.38. The area under the curve gives the total number of molecules. Thus, the area shaded in red shows the total number of molecules whose energy is above the Activation Energy.

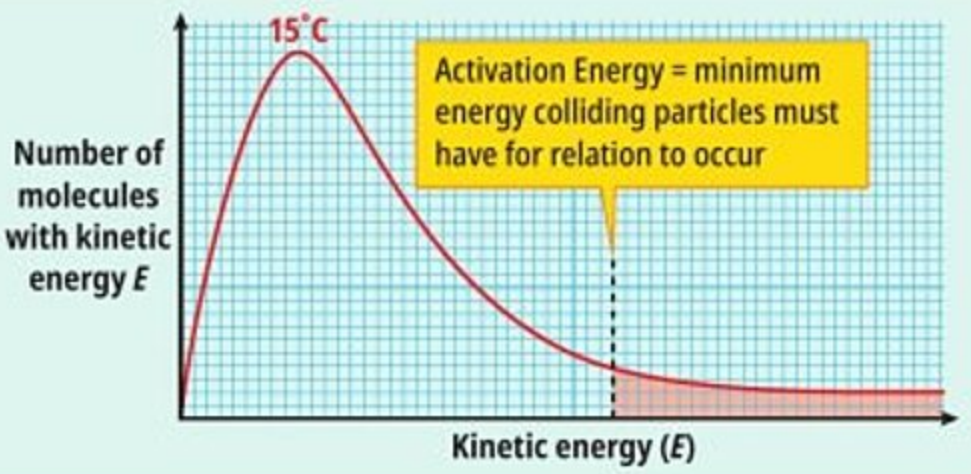

15°C
Activation Energy = minimum energy colliding particles must have for relation to occur
Number of molecules with kinetic energy E
Kinetic energy (E)

Figure 17.38 This graph shows the distribution of energies of the molecules in a sample of gas at a temperature of 15 °C.

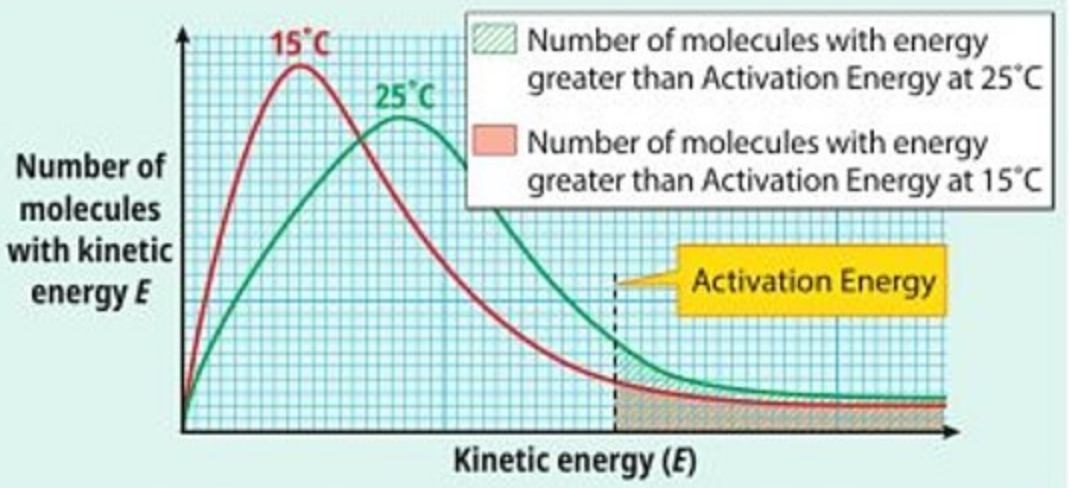

15°C
25°C
Number of molecules with energy greater than Activation Energy at 25°C
Number of molecules with energy greater than Activation Energy at 15°C
Activation Energy
Number of molecules with kinetic energy E
Kinetic energy (E)

Figure 17.39 Increasing the temperature causes a greater number of molecules to have energy in excess of the activation energy.

If the temperature of the gas is increased, the kinetic energies of the gas molecules will increase also due to the heat energy supplied. This will mean that a greater proportion of molecules will now have higher energies as shown in Figure 17.39. Note that there is an increase in the number of molecules at 25 °C that have energies about the Activation Energy. In other words, the green-shaded area is bigger than the red-shaded area.

- This distribution of energy among the molecules in a sample of gas explains why it is that not all the collisions between molecules bring about a reaction.
- When molecules with low energies collide, they simply bounce apart without any reaction taking place.
- It is only those molecules with high enough energies when they collide that form the products.
- A certain amount of energy is necessary for a chemical reaction to occur when molecules collide, i.e. for the collision to be effective.
- This energy is called the **Activation Energy** and is defined as follows:

Thus, the collision theory explains why reactions are faster at higher temperatures because a greater number of collisions reach the Activation Energy, i.e. more of the collisions have enough energy for the reaction to occur. In short, at higher temperatures there are more effective collisions.

Note: An increase in temperature does not change the size of the Activation Energy itself, since this size depends on the nature of the reactants, i.e. it depends on the particular reaction.

The **Activation Energy** is the minimum energy that colliding particles must have for a reaction to occur, i.e. the minimum energy required for effective collisions between particles to occur.

Example 19.7

Question

Give two reasons why the rate of a chemical reaction increases as the temperature rises.
Which of these reasons is the more significant? Why?

[LCH]

Answer

The rate of a chemical reaction increases as the temperature rises for the following two reasons:

1. There is an increased number of collisions since the moving molecules have more energy (they are moving faster) at the higher temperature.
2. More of the collisions are effective at the higher temperature, i.e. the colliding molecules have the minimum Activation Energy needed to react.

The more significant reason is the second one above. The reason why this is more significant is because, if molecules with low energies collide, they simply bounce apart without any reaction taking place. Thus, an increase in the number of collisions will not necessarily lead to the reaction taking place. The important thing is that the rise in temperature must be great enough to ensure that the colliding molecules have enough energy to reach the Activation Energy.

It is also generally the case that, for a particular temperature rise, the increase in the number of collisions is far exceeded by the increase in the fraction of those collisions that are effective.

The size of the Activation Energy depends on the nature of the reactants.

- Some reactions have a large Activation Energy. This means that these reactions are slow or may not occur at all, since only a small fraction of the particles have enough energy to supply the Activation Energy.
- In other cases, a greater fraction of the molecules have sufficient energy to supply the Activation Energy.
- This means that a greater fraction of the collisions are effective, i.e. these reactions are fast.

Activation Energy is often represented as shown in Figure 17.40.

This type of diagram is called a **Reaction Profile Diagram or Energy Profile Diagram**.

A **Reaction Profile Diagram (Energy Profile Diagram)** is a graph which shows the change in energy of a chemical reaction with time as the reaction progresses.

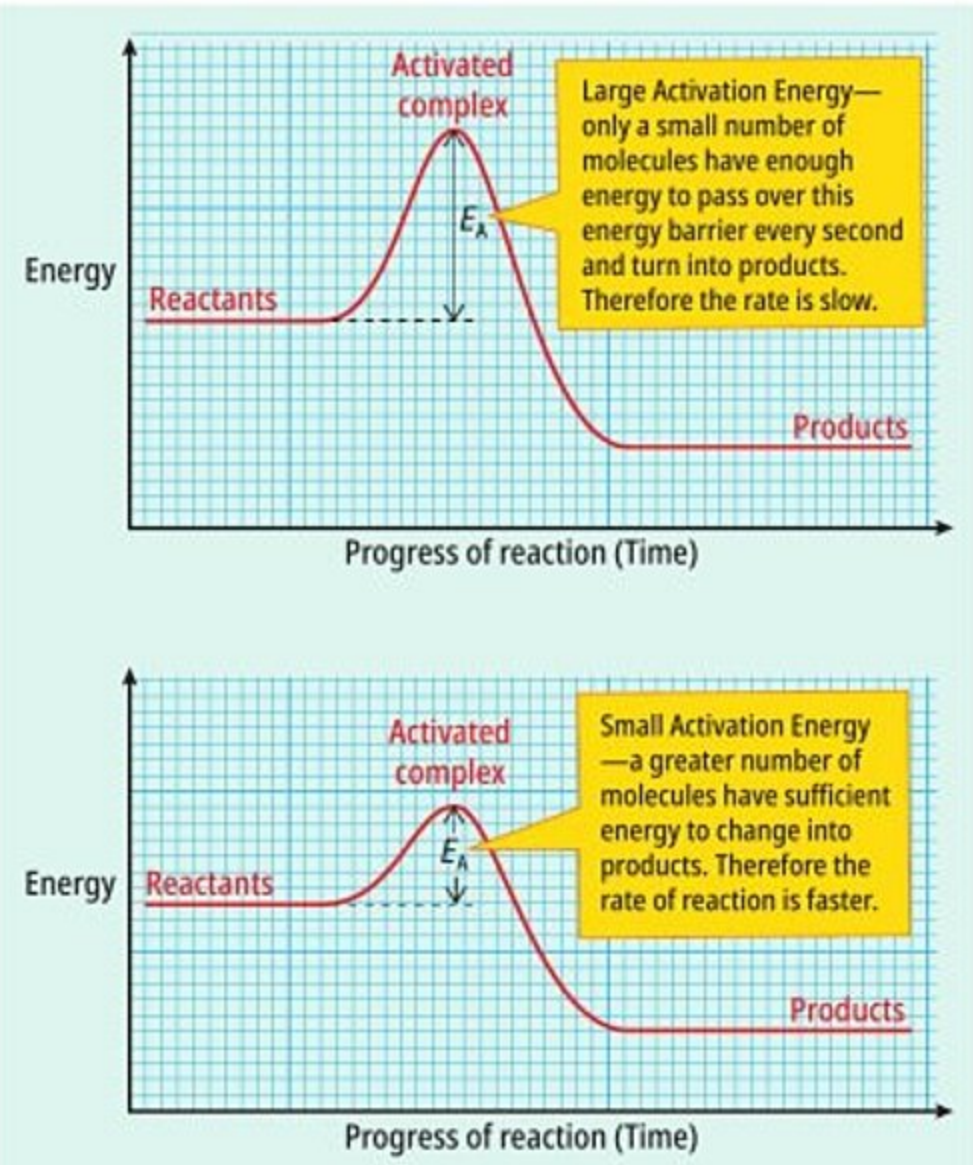

Activated complex
Large Activation Energy—only a small number of molecules have enough energy to pass over this energy barrier every second and turn into products. Therefore the rate is slow.
E_A
Energy
Reactants
Products
Progress of reaction (Time)
Activated complex
Small Activation Energy—a greater number of molecules have sufficient energy to change into products. Therefore the rate of reaction is faster.
E_A
Energy
Reactants
Products
Progress of reaction (Time)

Figure 17.40 The size of the activation energy determines the rate of reaction.

- Note from the diagram that the Activation Energy is the difference in energy between the average energy of the reactant molecules and the energy of molecules in the activated complex.
- The activated complex is simply an intermediate substance formed by the collision of molecules with enough energy to react.
- Reaction profile diagrams may be compared to a ball being rolled up a slope. If the ball has a lot of energy going up the slope, it may go over the top and roll down the other side, i.e. a chemical reaction occurs. If the ball has only a small amount of energy, it will only go a little way up the slope before falling back down.
- A chemical reaction that gives out heat is called an **exothermic** reaction. This means that the products have less energy than the reactants. The energy change between reactants and products is represented by the symbol ΔH, which is called the Heat of Reaction. For an exothermic reaction, ΔH represents the amount of heat given out. (We will be studying this in more detail in Chapter 21.) A reaction profile diagram for an exothermic reaction is shown in Figure 17.41.

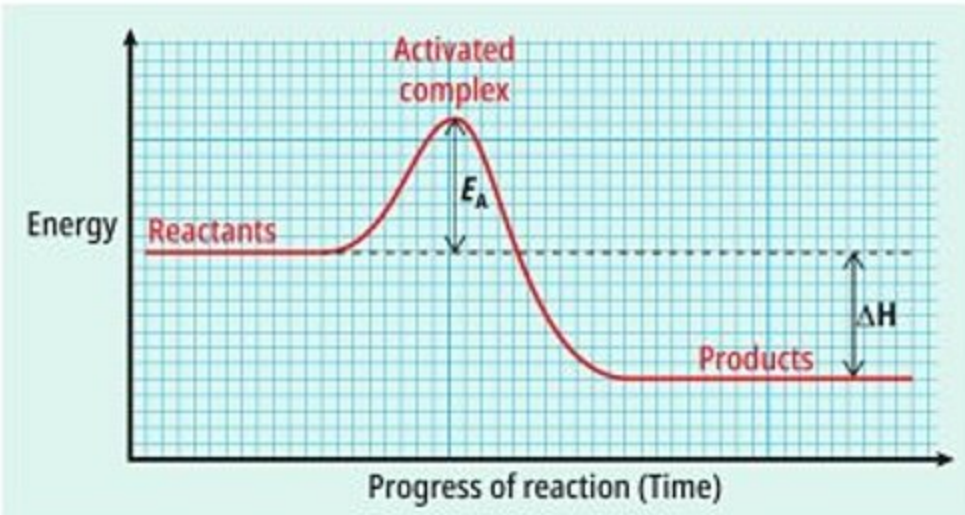


Figure 17.41 A reaction profile diagram for an exothermic reaction. Note that the products have less energy than the reactants. The energy given out is represented by the symbol ΔH.

A chemical reaction that takes in heat energy is called an **endothermic** reaction. In this case the products have more energy than the reactants. An endothermic reaction may also be represented by a Reaction Profile Diagram, Figure 17.42.

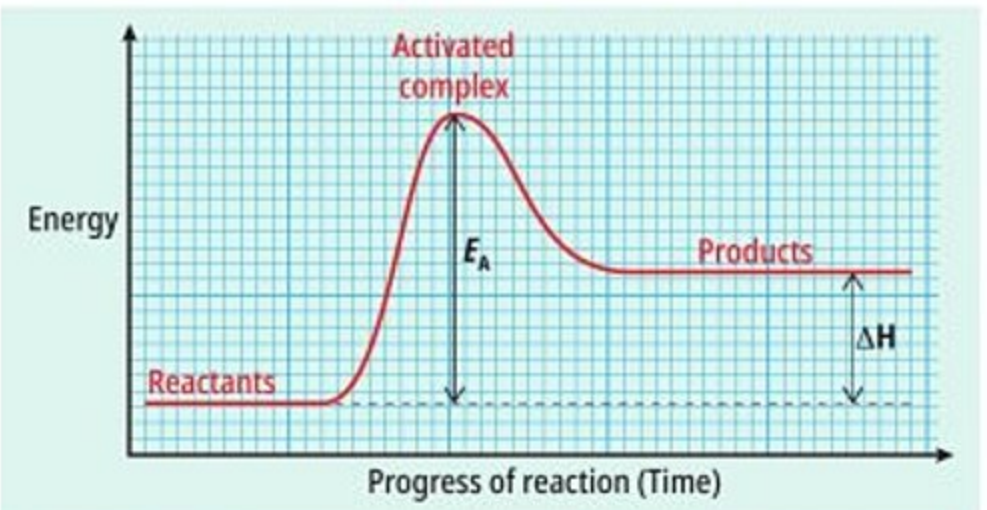


Figure 17.42 A reaction profile diagram for an endothermic reaction. Note that the products have more energy than the reactants. The energy taken in is represented by the symbol ΔH.

We have already discussed how the Collision Theory explains how a rise in temperature increases the rate of reaction. This theory may also be used to explain why the other factors that we have studied in this chapter affect the rate of a reaction.

(i) Nature of reactants: Reactions with covalent compounds involve bond-breaking taking place during a collision. This breaking of bonds requires energy and hence these types of reactions have much higher activation energies than reactions which merely involve oppositely-charged ions colliding with each other in solution.

(ii) Particle size: The smaller the particle size, the more surface area is exposed and, therefore, the greater the number of collisions taking place. Since the number of collisions that take place is greatly increased, the number of these collisions that are effective will also increase.

(iii) Concentration: If the concentration of the reactants is increased, the number of collisions will also be increased because the particles are closer together. Therefore, the number of effective collisions will be increased, giving rise to an increased rate of reaction.

In some cases, an increase in concentration may not always affect the rate, Figure 17.43. For example, we have seen that the rate of reaction increases when a more concentrated solution of HCl is used to investigate the rate of reaction between HCl and Mg. However, if you keep increasing the concentration of HCl, a further increase may not necessarily increase the rate of reaction as the maximum number of collisions between hydrogen ions and the magnesium atoms on the surface of the magnesium are already taking place. In other words, the surface of the Mg metal is already saturated with hydrogen ions.

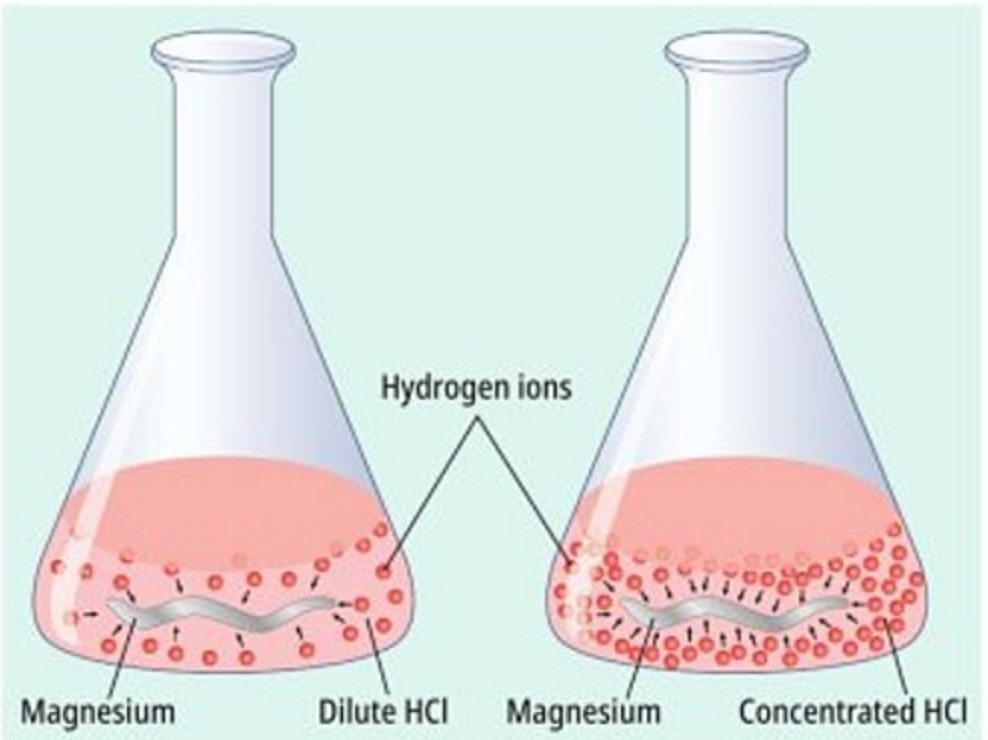


Figure 17.43 When the HCl solution is already very concentrated, a further increase in concentration may not increase the rate of the reaction due to a type of 'saturation effect' at the surface of the metal. In other words, the maximum number of collisions between hydrogen ions and the magnesium atoms are taking place.

Another example of a reaction in which increasing the concentration does not affect the rate is the addition of silver nitrate solution to a solution containing chloride ions. You will recall that a precipitate of silver chloride forms immediately (Chapter 5). The reaction is very fast (or instantaneous) on mixing the two solutions. Therefore, even if you change the concentration of one or more of the reactants, the time to form the precipitate won't change.

(iv) Catalyst: A catalyst works by providing an alternative reaction pathway with a lower activation energy, Figure 17.44. Therefore, more reactant molecules now possess the energy required for effective collisions to occur. Therefore, the rate of reaction increases.

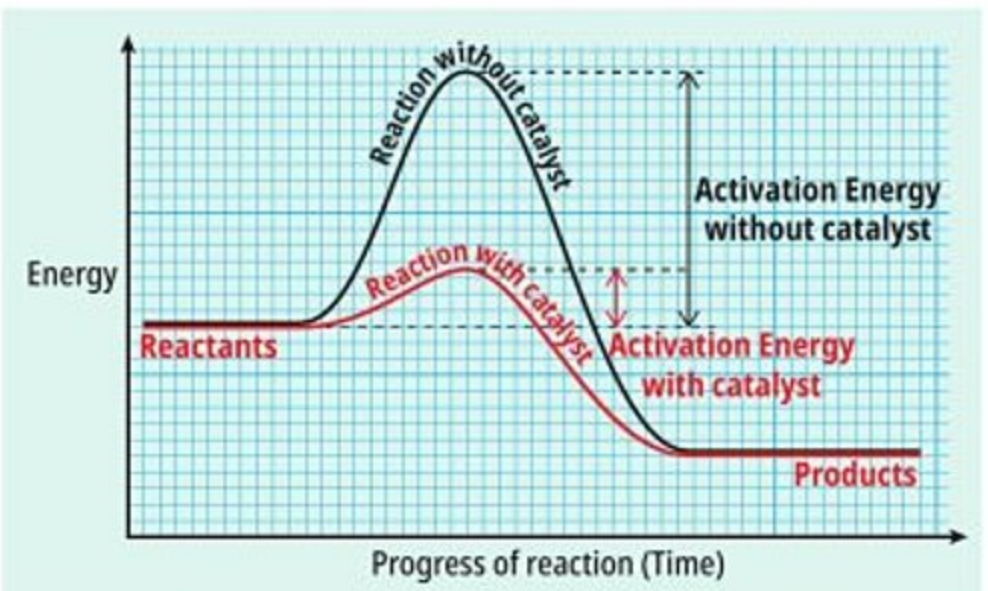


Figure 17.44 A catalyst reduces the activation energy for a reaction. In this case, the reaction profile diagram is shown for both a catalysed and uncatalysed **exothermic** reaction.

A reaction profile diagram may also be drawn to represent an endothermic reaction that is both catalysed and uncatalysed, Figure 17.45.

(v) Pressure: As already discussed, for reactions in which all the reactants and products are gases, when you increase the pressure of the gaseous reactants, you compress the gas particles into a smaller volume. Therefore, the gas particles are closer together and will collide more frequently with each other. Since the particles collide more frequently with each other, there is a higher chance that more collisions will be effective and form products. Therefore, the reaction rate increases.

In general, for all-gaseous reactions, an increase in pressure results in an increase in reaction rate.

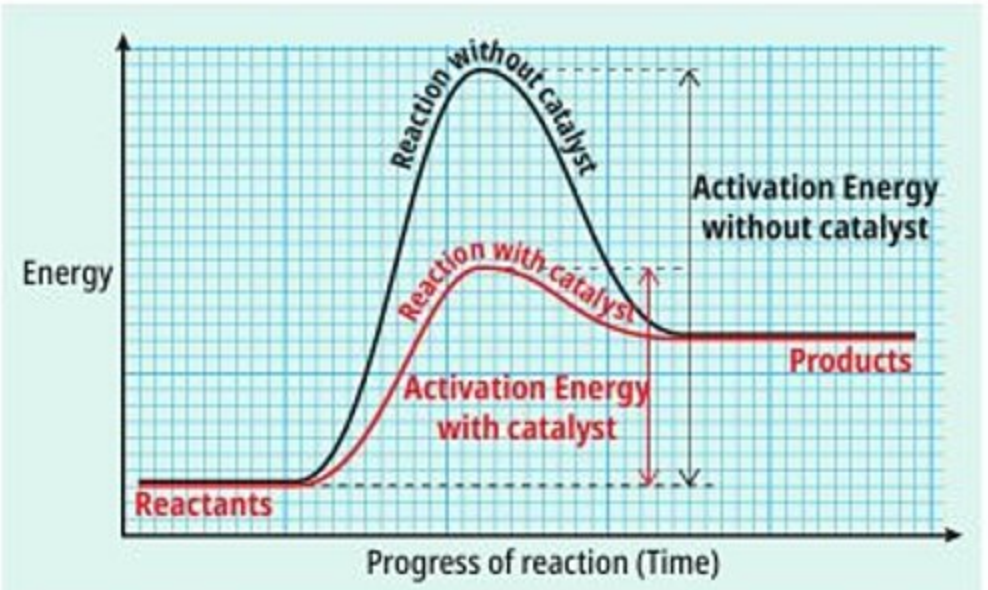


Figure 17.45 A reaction profile diagram is shown for a catalysed and uncatalysed **endothermic** reaction.

TEST YOURSELF: Attempt Questions 17.2–17.3 and W17.3–W17.24.

Study Example 17.4 in the online resources.

Summary What I should know

- The rate of reaction is defined as the change in concentration per unit time of any one reactant or product.
- The instantaneous rate of reaction is the rate of reaction at any one particular time during the reaction.
- The instantaneous rate is determined by measuring the slope of the tangent to the curve at that instant.
- By experiment, it is found that the rate of a reaction depends on the nature of the reactants, the particle size, the concentration, the temperature, the presence of a catalyst and pressure (for gaseous reactions).
- A catalyst is a substance that alters the rate of a chemical reaction but is not consumed in the reaction.
- Homogeneous catalysis is catalysis in which the reactants and the catalyst are in the same phase, i.e. there is no boundary between the reactants and the catalyst.
- Heterogeneous catalysis is catalysis in which the reactants and the catalyst are in different phases, i.e. there is a boundary between the reactants and the catalyst.
- Autocatalysis is catalysis in which one of the products of the reaction acts as a catalyst for the reaction.
- The Intermediate Formation Theory and the Surface Adsorption Theory are used to explain how catalysts work.
- A catalytic converter is a device in the exhaust system of a motor vehicle that contains catalysts to convert pollutants in the exhaust gases to less harmful substances.
- A catalyst poison is a substance that makes a catalyst inactive.
- An effective collision is one that results in the formation of products.
- The Activation Energy is the minimum energy that colliding particles must have for a reaction to occur, i.e. the minimum energy required for effective collisions between particles to occur.

Learning outcomes

At the end of this chapter, I should be able to:			
Define and explain rate of reaction, giving examples of slow and fast reactions.	⬡	⬡	⬡
Investigate the factors that affect rates of reaction and interpret rates of reaction graphs.	⬡	⬡	⬡
Describe the mechanisms of catalysis.	⬡	⬡	⬡
Describe Collision Theory and apply it to explain the factors that affect the rates of reactions.	⬡	⬡	⬡
Compare the energy profile diagrams of catalysed and uncatalysed reactions, for both exothermic and endothermic reactions.	⬡	⬡	⬡

Chapter review questions

17.1 Define rate of reaction.

Describe simple experiments, one in each case, to illustrate the following statements.

(a) 'Ionic reactions in solution are almost instantaneous.'

(b) 'Particle size can have a significant effect on reaction rate.'

Excluding particle size and the ionic or covalent nature of the reactants, list three factors that can affect the rate of a chemical reaction. [LCH]

17.2 **(a)** Distinguish between the terms *average rate* and *instantaneous rate*.

(b) What is a catalyst?

(c) In coal mines, there is a great danger that coal dust may catch fire and start an explosion. Why is coal dust more dangerous than coal?

(d) Hydrogen gas is evolved more quickly when zinc powder is reacted with hydrochloric acid than when granulated zinc is used. Explain this observation.

(e) Explain the term *autocatalysis*. Give an example of a reaction that could be used to demonstrate autocatalysis.

(f) Perishable foods stay fresher for longer when stored in a fridge than in a warm room. Explain this observation.

(g) Write down the balanced equation to describe the reaction between sodium thiosulfate and hydrochloric acid.

(h) Catalytic activity is associated particularly with transition metals and their compounds. Suggest a reason for this.

(i) Give two examples of enzymes and state the substances on which they act.

(j) Give two reasons why raising the temperature usually increases the rate of a chemical reaction. [LCH]

17.3 Hydrogen peroxide decomposes rapidly at room temperature in the presence of certain catalysts, according to the equation:

$2H_2O_2 \rightarrow 2H_2O + O_2$

In one such experiment, 2 g of manganese dioxide were added to 20 cm^3 of a solution of hydrogen peroxide. The volume of oxygen liberated was measured at intervals, with the following results:

Time (secs)	0	15	30	45	60	90	120	150	180	210	240
Vol. of O_2 (cm^3)	0	60	110	134	150	170	184	193	197	200	200

(a) Using graph paper, plot the volume of oxygen liberated against time.

(b) After what time could the reaction be said to be complete?

(c) What fraction of the hydrogen peroxide decomposed in the first minute?

(d) Explain why the rate of the reaction gets slower as the reaction proceeds.

(e) If this reaction were carried out at a temperature higher than room temperature, would the curve lie above or below the curve you have drawn at room temperature? Explain fully the reason for your answer.

(f) Explain why the decomposition of hydrogen peroxide at room temperature is very slow in the absence of a catalyst. [LCH]

18 Chemical Equilibrium

OBJECTIVES

- To give students an understanding of the concept of chemical equilibrium.
- To provide students with the opportunity to carry out laboratory work involving a reaction at chemical equilibrium.
- To ensure that students know how to solve problems involving reactions at chemical equilibrium.

18.1 Introduction: What is equilibrium?

If you look up the word 'equilibrium' in a dictionary, you will find it explained using words such as 'state of balance'.

Imagine a metre stick is suspended at its point of balance (centre of gravity). The stick is said to be balanced or in equilibrium, Figure 18.1. Note that the stick is not tipping over to one side: it is staying still, or static. Therefore, this type of equilibrium is called **static equilibrium**. The entire system is not moving. Static equilibrium occurs when an object is at rest and does not move because all the forces acting on it are balanced.

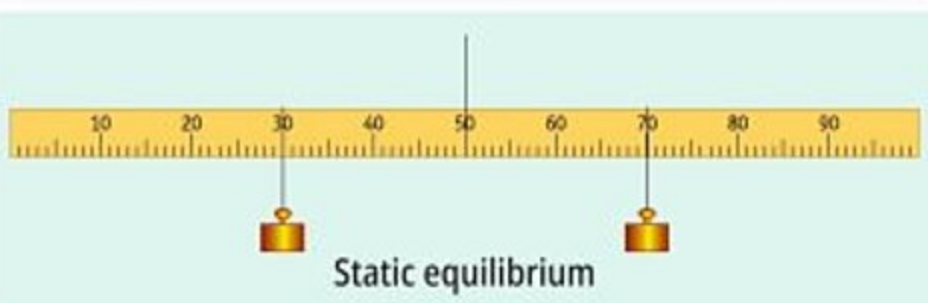


Figure 18.1 The metre stick does not move because the forces acting on it are balanced. Since the metre stick does not move, this type of state of balance is called static equilibrium.

Now imagine runners on a treadmill, as in Figure 18.2. They are running forward, but the treadmill belt is moving backward at the same speed. Because they are moving at the same speed as the treadmill, each runner stays in the same spot. The two opposing motions balance each other, so there is no overall change in position. This is an example of **dynamic equilibrium**. The word 'dynamic' implies movement.

Figure 18.2 The photograph shows an example of dynamic equilibrium. The speed of each runner in the forward direction is equal to the speed of the belt in the opposite direction. The word 'equilibrium' means 'state of balance'.

Another example of a dynamic equilibrium is walking down an escalator at the same speed as it is moving up. There is no overall change in position because the two opposing motions are balanced.

In this chapter, we will consider chemical reactions in which a state of dynamic equilibrium exists.

18.2 What is chemical equilibrium?

When magnesium ribbon is burned in air, a very bright light is observed and a white substance called magnesium oxide is formed. We may write this reaction as follows:

$$\underset{\text{magnesium}}{2Mg} + \underset{\text{oxygen}}{O_2} \rightarrow \underset{\text{magnesium oxide}}{2MgO}$$

This reaction is a one-way process – it is very difficult to turn the magnesium oxide back into magnesium and oxygen. Chemists often say that the reaction 'goes to completion'. In other words, the reactants are completely converted to products.

However, by experiment, it is found that there are many chemical reactions that do not 'go to completion'. One example of this is the reaction between hydrogen gas and nitrogen gas.

In 1908 two German chemists, Fritz Haber and Carl Bosch discovered that nitrogen gas and hydrogen gas reacted to form ammonia, Figure 18.3.
Ammonia is a gas used in the manufacture of fertilisers, cleaning agents, explosives and nylon.

$$\underset{\text{nitrogen}}{N_2} + \underset{\text{hydrogen}}{3H_2} \rightarrow \underset{\text{ammonia}}{2NH_3}$$

Figure 18.3

Fritz Haber (1868–1934) **Carl Bosch** (1874–1940)

The process to manufacture ammonia from nitrogen and hydrogen is called the Haber process or, more correctly, the Haber-Bosch process, after the chemist (Fritz Haber) and the chemical engineer (Carl Bosch) who developed the process.

However, Haber discovered that the reaction did not go completely from left to right. He found that some of the ammonia that was formed actually decomposed to give back the nitrogen and hydrogen. In other words, he found that the above reaction takes place in both directions:

- In the forward direction, it takes place to form ammonia.
- In the backward direction, it takes place so that ammonia breaks down to form nitrogen and hydrogen.

Since the above reaction takes place both in the forward and backward directions, it is said to be **reversible**.

A **reversible reaction** is one in which the products react to give back the reactants, i.e. the reaction is going in both directions.

Reversible reactions are also called equilibrium reactions and are indicated using the equilibrium arrow sign (⇌).

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

Chemical reactions such as the above involve a **dynamic equilibrium**. This means that nitrogen and hydrogen are continuously reacting together to form ammonia, while ammonia is continuously decomposing to form nitrogen and hydrogen. When this state of equilibrium has been reached, it is found that the rate of the forward reaction is the same as the rate of the backward reaction. Therefore, there is no change in the overall amounts of nitrogen or hydrogen or ammonia present in the container.

In general, if reactants A and B react together to form products C and D and a state of equilibrium is reached, we can represent this as follows:

$$\underbrace{A + B}_{\text{reactants}} \underset{\text{backward reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} \underbrace{C + D}_{\text{products}}$$

At equilibrium, the rate of the forward reaction is equal to the rate of the backward reaction, i.e. $R_f = R_b$

$$\underbrace{A + B}_{\text{reactants}} \underset{R_b}{\overset{R_f}{\rightleftharpoons}} \underbrace{C + D}_{\text{products}}$$

Chemical equilibrium is a state of dynamic balance in a reversible reaction where the rate of the forward reaction is the same as the rate of the backward reaction.

Visualising chemical equilibrium

Studying Figure 18.4 will help you to understand the concept of equilibrium. This graph describes what happens to the concentrations of reactants and products when nitrogen gas and hydrogen gas are placed in a sealed container.

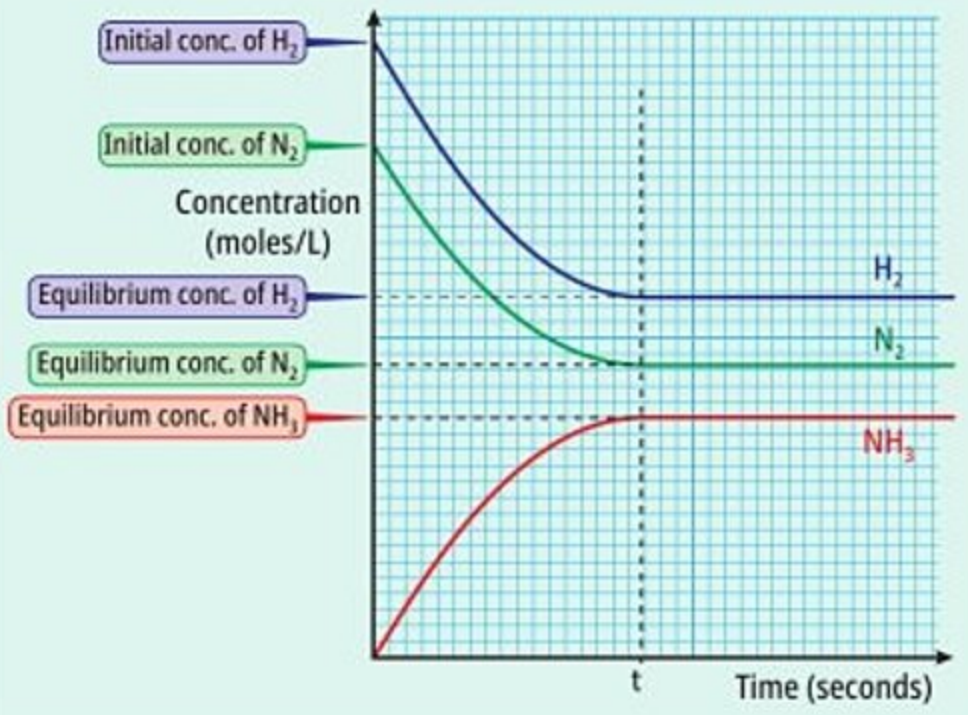


Figure 18.4 When equilibrium is reached at time ***t*** the concentrations of reactants and products become steady and no longer change with time.

Note the following:

- The initial concentrations of nitrogen and hydrogen have fixed values depending on the number of moles of these gases placed in the sealed container.
- The initial concentration of ammonia is zero since the nitrogen and hydrogen have not yet reacted together to form ammonia.
- As the reaction proceeds, the rate of the forward reaction decreases (since the concentrations of the nitrogen and hydrogen are decreasing) and the rate of the backward reaction increases (since the concentration of the ammonia is increasing) until eventually, at time ***t***, the rate of the forward reaction becomes equal to the rate of the backward reaction.
- At this stage, note carefully in Figure 18.4, the concentrations of all three substances in the container become constant due to the fact that the nitrogen and hydrogen are continuously reacting to form ammonia and the ammonia is continuously decomposing to form nitrogen and hydrogen.
- When this stage is reached, the situation in the container is described as a **dynamic equilibrium** because the nitrogen and hydrogen are continuously forming ammonia, while the ammonia is continuously decomposing to form nitrogen and hydrogen. The term *dynamic* also indicates that neither the forward nor the backward reaction has actually stopped – both are still occurring.

In a **dynamic state** the reactants are continuously forming products and the products are continuously forming reactants.

A **dynamic chemical equilibrium** is the equilibrium that exists in a closed system of a chemical reaction when the rate of the forward reaction is equal to the rate of the backward reaction. The concentrations of the reactants and products remain the same.

When the rate of the forward reaction is equal to the rate of the backward reaction, the two reactions balance out and hence the name **dynamic chemical equilibrium** is used to describe what is happening.

The initial state and the dynamic equilibrium state for the above reaction are shown in Figure 18.5.

Initially, the gases are fed into the sealed metal container (reactor) in which the reaction takes place. At this stage, the reactor contains only molecules of nitrogen and hydrogen as they have not yet reacted. However, at equilibrium, the reactor contains a mixture of nitrogen, hydrogen and ammonia.

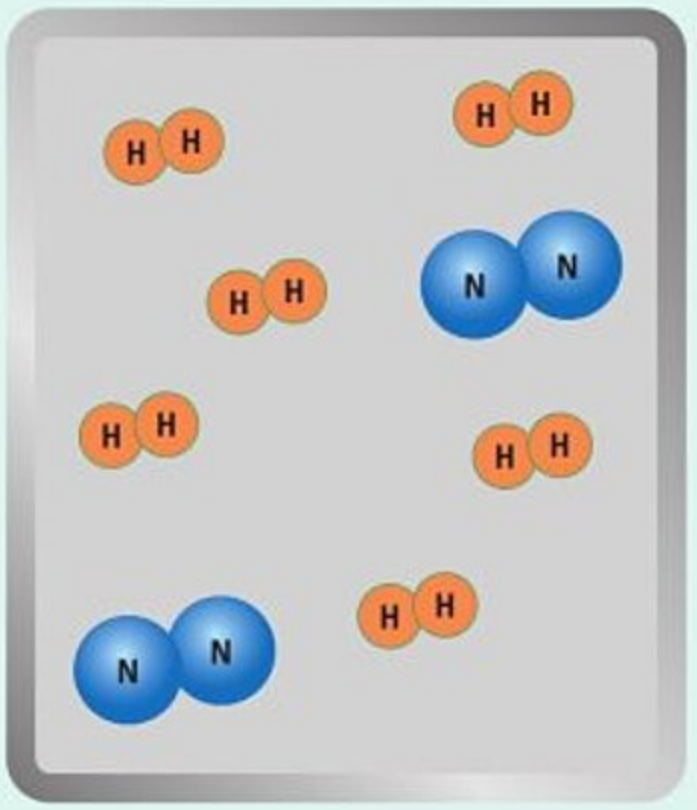


Figure 18.5 (a) The initial state when hydrogen and nitrogen are mixed.

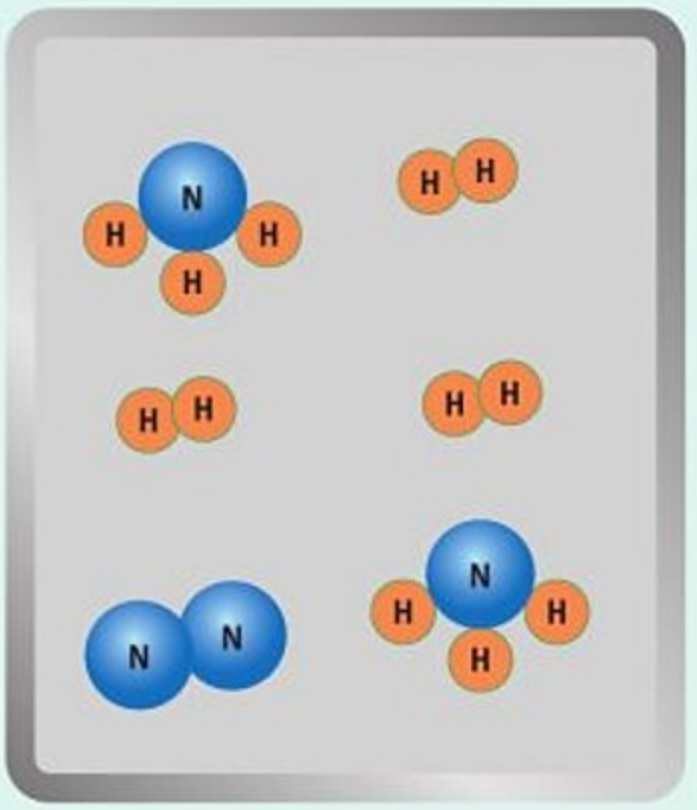


Figure 18.5 (b) The dynamic equilibrium state when the rate of the forward reaction is equal to the rate of the backward reaction. Note that at equilibrium, both reactants and products are present.

The container in which chemical reactions involving gases are carried out is usually sealed to ensure that gases cannot escape as equilibrium is being established. This system is called a **closed system**.

Note the following:

- A **closed system** means that no matter can enter or leave the container. In other words, the total amount of reactants and products remains constant within the system to allow a state of chemical equilibrium to be reached.
- In a **closed system** the concentrations of reactants and products remain constant at equilibrium because no substances can enter or leave the system. The concentrations are constant because the system is sealed and this prevents the addition or removal of reactants or products.
- Even though no matter can enter or leave a closed system, energy (e.g. heat or light) can still be exchanged with the surroundings in a closed system.
- The state of equilibrium can be achieved from either direction of the reaction. In other words, if ammonia were placed in the reactor initially, the same state of equilibrium would be established as if you started with nitrogen and hydrogen.

18.3 Le Chatelier's Principle

Many chemical processes involve equilibrium reactions. Therefore, for economic reasons, it is important for chemists to try to shift the equilibrium as much as possible to the right, i.e. to maximise the amounts of products formed. A French chemist called Henri Le Chatelier, Figure 18.6, studied many equilibrium reactions.

Figure 18.6

Henri Le Chatelier
(1850–1936)

Henri Le Chatelier was a very practical industrial chemist who worked as a mining engineer prior to his appointment in 1877 as Professor of General Chemistry at the School of Mines in Paris. He was particularly interested in finding ways to increase yields in industrial processes. This helped lead him to the discovery of the principle that bears his name.

In 1888 Le Chatelier put forward a rule that allowed chemists to predict the direction taken by an equilibrium reaction if the conditions of the reaction were changed. This rule is known as Le Chatelier's Principle and may be stated as follows:

Le Chatelier's Principle states that if a stress is applied to a system at equilibrium, the system readjusts to relieve the stress applied.

In the above statement of Le Chatelier's Principle, the word 'stress' simply means a change in the conditions of the reaction, such as:

- A change in the concentration of either reactants or products
- A change in pressure
- A change in temperature.

In simple language, Le Chatelier's Principle tells us that if we change the conditions of a reaction that has reached a state of equilibrium, the equilibrium will be shifted in such a direction that the effect of the change will be minimised. When this has been achieved, a new state of equilibrium will have been set up.

Demonstrating Le Chatelier's Principle

To demonstrate Le Chatelier's Principle, consider the reaction in which two molecules of nitrogen dioxide, NO_2, join together to form a molecule of dinitrogen tetroxide, N_2O_4. Both of these substances are gases, as indicated in the following equation:

$$2NO_{2\,(g)} \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} N_2O_{4\,(g)}$$

nitrogen dioxide **(dark brown)** — dinitrogen tetroxide **(colourless)**

The forward reaction gives out heat (an **exothermic** reaction) and the backward reaction takes in heat (an **endothermic** reaction). Chemists use the symbol ΔH to indicate whether a reaction gives out heat or takes in heat. For example, the above equation could also be written:

$$2NO_{2\,(g)} \rightleftharpoons N_2O_{4\,(g)} \qquad \Delta H = -58.1 \text{ kJ mol}^{-1}$$

The negative sign indicates that the reaction gives out heat in the forward direction.

» You will learn more about ΔH in Chapter 21.

The effect of change of temperature on this reaction is illustrated in Figure 18.7.

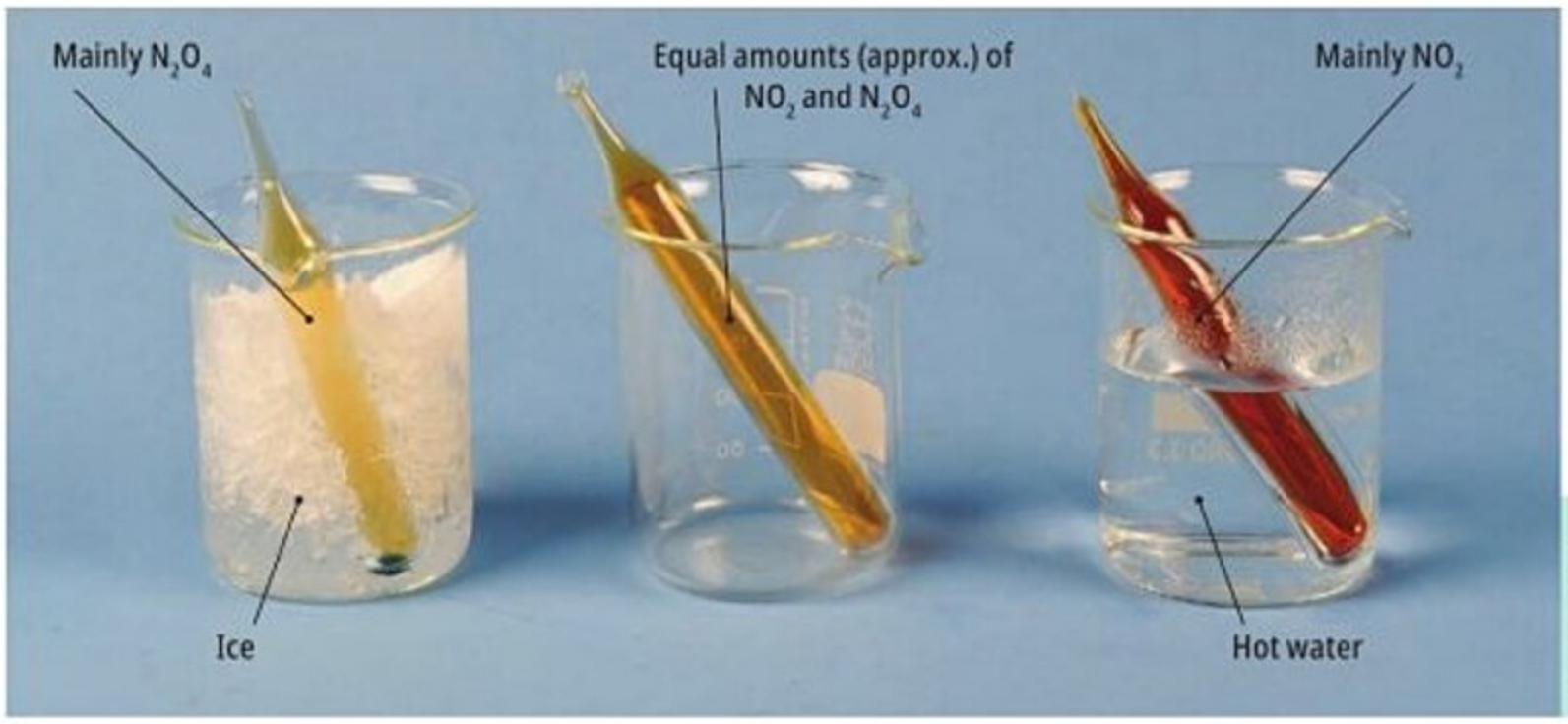


Figure 18.7 An experiment to demonstrate Le Chatelier's Principle

The three test-tubes contain an equilibrium mixture of nitrogen dioxide gas and dinitrogen tetroxide gas. The middle test-tube is at room temperature and contains an approximate equal mixture of the two gases. Hence the light-brown colour.

The test-tube on the left is placed in ice. The lowering of the temperature constitutes a stress.

To minimise the effect of the lowering of the temperature, the equilibrium is shifted in the direction that produces heat (Le Chatelier's Principle). Therefore, the forward reaction predominates (exothermic) and this results in the production of more dinitrogen tetroxide.

Therefore the brown colour becomes pale yellow.

If you lowered the temperature even more – using liquid nitrogen – the contents of the test-tube would become almost colourless.

$$2NO_{2\,(g)} \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} N_2O_{4\,(g)}$$

nitrogen dioxide **(dark brown)** ⇌ dinitrogen tetroxide **(colourless)**

The test-tube on the right is placed in hot water. In order to absorb the stress of increased temperature, the reaction that absorbs heat will predominate, i.e. the equilibrium is shifted in the backward direction as predicted by Le Chatelier's Principle. Therefore, more nitrogen dioxide is produced.

Therefore the contents of the test-tube turn dark-brown.

$$2NO_{2\,(g)} \underset{\text{endothermic}}{\overset{\text{exothermic}}{\rightleftharpoons}} N_2O_{4\,(g)}$$

Effect of pressure change on reactions involving gases

In reactions in which all the reactants and products are gases, Le Chatelier found that in certain cases he was able to use changes in pressure to shift the direction of equilibrium in either the forward or backward direction. This may be illustrated by the reaction between nitrogen gas and hydrogen gas to form ammonia gas, Figure 18.8.

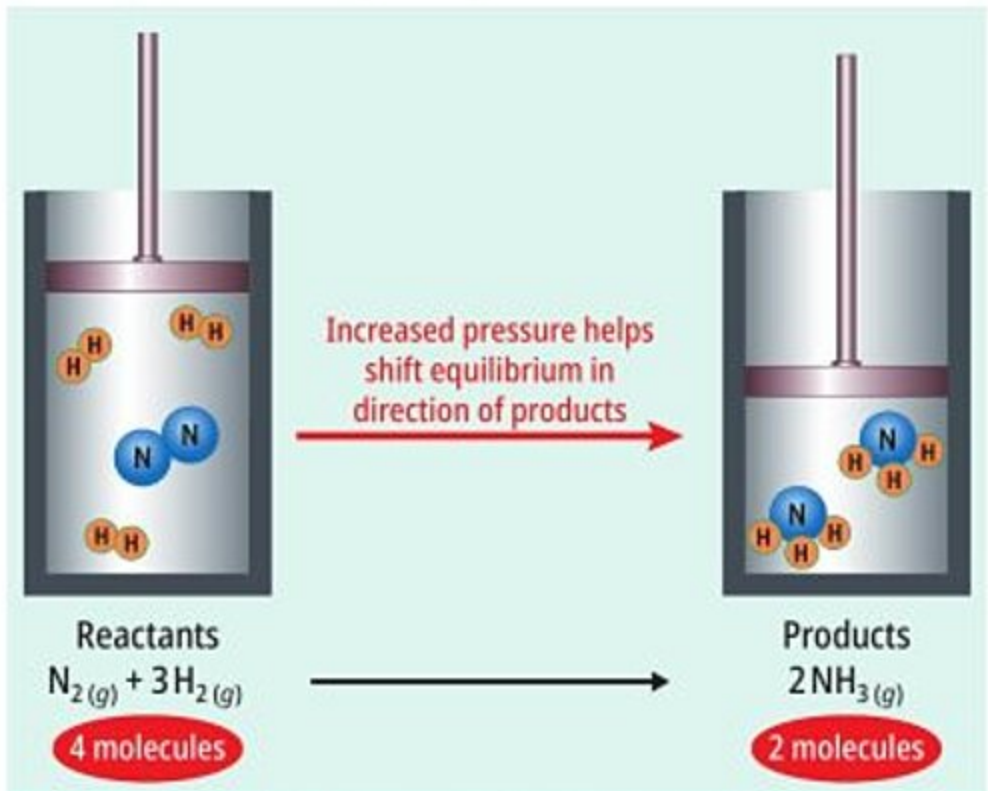


Figure 18.8 If the pressure is increased, the equilibrium shifts to the side of the equation that has the smaller number of molecules. The smaller number of molecules occupies less volume and this helps to absorb the stress of increased pressure.

Le Chatelier's findings may be summarised as follows:

Le Chatelier's Principle predicts that in an all-gaseous reaction, an increase in pressure will favour the reaction that brings about a reduction in volume. This means it will shift towards the side with the smaller number of molecules.

A change in the pressure on a system affects only an equilibrium reaction that has an unequal number of molecules of gaseous reactants and products. In Figure 18.8, the increase in pressure is relieved by the equilibrium being shifted to the side with the smaller number of molecules.

In all gaseous reactions in which there is the same total number of molecules on both sides of the equation, a change in pressure will have no effect on the position of equilibrium.

We have already seen in Chapter 17 that a catalyst alters the rate of a chemical reaction. In the case of a reaction that has reached a state of dynamic equilibrium, a catalyst increases (or in some cases decreases) the rate of both the forward reaction and the reverse reaction by the same amount. In other words, the catalyst enables the system to reach a state of equilibrium in a shorter time. However, adding a catalyst to an equilibrium reaction does not affect the position of equilibrium in the reaction or the composition of the equilibrium mixture. Thus, a catalyst does not alter the yield of product in an equilibrium reaction. In short, **a catalyst speeds up the rate at which equilibrium is reached but it does not change the position of equilibrium**.

Example 18.1

Question

The following reaction occurs in a closed vessel at a certain temperature. The forward reaction is exothermic.

$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$

What would be the effect on the concentration of PCl_5 in the equilibrium mixture of:

(i) introducing more PCl_3 into the mixture, **(ii)** increasing the pressure, **(iii)** increasing the temperature? [LCH]

Answer

(i) If more PCl_3 is introduced into the container, the equilibrium will shift to the right to absorb the increase. Therefore, the concentration of PCl_5 will increase.

(ii) Note that all of the substances in the above reaction are gaseous. There are two molecules on the left-hand side of the equation but only one on the right-hand side of the equation. If we increase the pressure, the equilibrium shifts to the side that has the smaller number of molecules (in accordance with Le Chatelier's Principle). Therefore, the equilibrium shifts to the right-hand side. Thus, the concentration of PCl_5 increases.

(iii) We are told that the forward reaction is exothermic. This implies that the backward reaction is endothermic.

$$PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$$

exothermic (forward) / endothermic (backward)

If the temperature is increased, the equilibrium will be shifted in the backward direction in order to absorb this heat. Therefore, the concentration of PCl_5 will decrease.

18.1 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 18 in the Student Laboratory Notebook.

Student Experiment No. 18

To investigate how changes in (a) concentration and (b) temperature can affect the state of equilibrium in the reaction between iron (III) chloride and potassium thiocyanate

Introduction

In this experiment we will investigate the effect of changes in (a) concentration and (b) temperature on the state of equilibrium in the following reaction:

$$\underset{\text{yellow}}{Fe^{3+}} + CNS^- \rightleftharpoons \underset{\text{red}}{Fe(CNS)^{2+}}$$

We use iron (III) chloride ($FeCl_3$) as the source of the Fe^{3+} ions and potassium thiocyanate (KCNS) as the source of the CNS^- ions. Fe^{3+} ions are yellow and CNS^- ions are colourless. However, when the two ions combine, an equilibrium reaction is set up involving the production of the blood-red ferrothiocyanate ion. This is a complex ion of formula $Fe(CNS)^{2+}$.

Part (a) To investigate the effect of concentration

Key steps in procedure

- About 5 cm^3 of iron (III) chloride solution and one drop of potassium thiocyanate solution are mixed in a test-tube.

Observation

A red colour is observed, Figure 18.9.

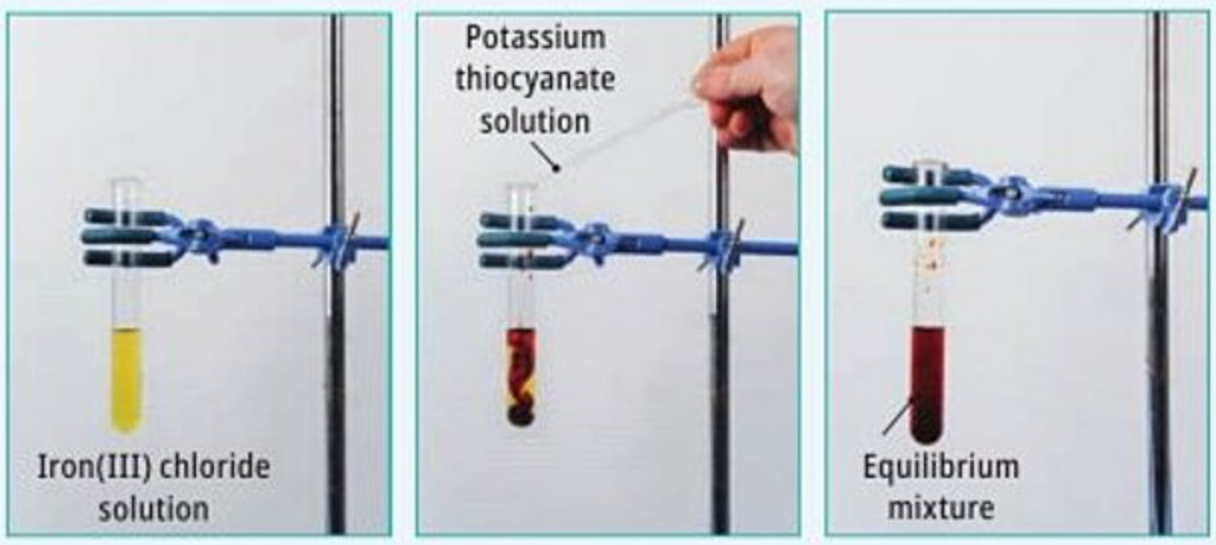


Figure 18.9 The red colour is due to the presence of the $Fe(CNS)^{2+}$ ion. This means that the equilibrium lies on the right-hand side of the equation shown above.

Explanation

The red colour is caused by the formation of $Fe(CNS)^{2+}$ as follows:

$$\underset{\text{yellow}}{FeCl_3} + \underset{\text{colourless}}{CNS^-} \rightleftharpoons \underset{\text{red}}{Fe(CNS)^{2+}} + 3Cl^-$$

Since the red colour is observed, the equilibrium must lie on the right-hand side of the above equation.

- Some dilute hydrochloric acid is added until the red colour disappears.

Explanation

In keeping with Le Chatelier's Principle, the red colour disappears as the equilibrium is shifted to the left-hand side to absorb the Cl^- ions added.

- Add some potassium thiocyanate solution.

Observation

A red colour is observed.

Explanation

In keeping with Le Chatelier's Principle, the solution becomes red because the equilibrium is shifted to the right-hand side to absorb the CNS^- ions added.

Part (b) To investigate the effect of temperature

In this part of the experiment, we will investigate the effect of **temperature** on the equilibrium:

$$Fe^{3+} + CNS^- \underset{\textbf{endothermic}}{\overset{\textbf{exothermic}}{\rightleftharpoons}} Fe(CNS)^{2+}$$

yellow colourless red

Key steps in procedure

- Mix together about 10 cm^3 of a solution of iron(III) chloride and a drop or more of potassium thiocyanate solution in a test-tube.

  Observation

  A red colour is formed.

  Explanation

  The equilibrium lies on the right-hand side of the above equation.

- The solution is divided among three test-tubes. One test-tube is placed in hot water, one test-tube is placed in ice, and the third test-tube is left at room temperature.

  Observation

  - The red colour changes to yellow in the test-tube placed in hot water, Figure 18.10. The colour change is difficult to see.
  - The yellow colour changes to red in the test-tube placed in ice. This colour change is difficult to see.

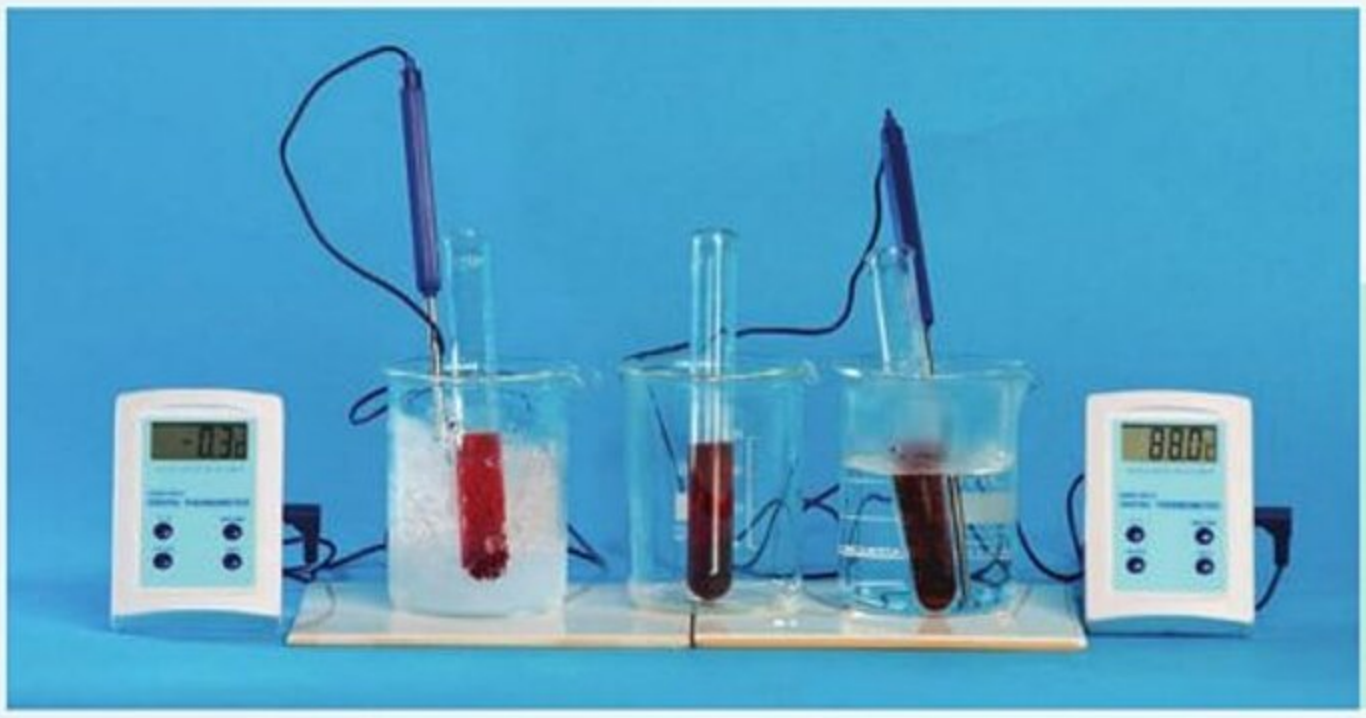


Figure 18.10 The red colour changes to yellow when the equilibrium mixture is placed in boiling water. The red colour becomes more intense when the equilibrium mixture is placed in ice.

Explanation

In the case of the test-tube placed in hot water, the equilibrium shifts to the left (direction of endothermic reaction) in order to absorb the added heat. Therefore, the red colour changes to yellow. This is in keeping with Le Chatelier's Principle.

In the case of the test-tube placed in iced water, the equilibrium shifts to the right (direction of exothermic reaction) in order to replace the heat that has been removed. Therefore, the colour changes to red. This is in keeping with Le Chatelier's Principle.

We conclude that adding heat favours the direction of the endothermic reaction (in which heat is absorbed) and removing heat favours the direction of the exothermic reaction (in which heat is liberated).

A video of this experiment is available on FolensHIVE

18.4 Using Le Chatelier's Principle to optimise product yield

As a case study, we now consider how Le Chatelier's Principle is applied to maximise yield in the industrial manufacture of ammonia. Ammonia is one of the most important chemicals manufactured by the chemical industry. Ammonia is used to manufacture fertilisers, explosives and cleaning agents. Approximately 80% of all ammonia produced is used to manufacture fertilisers, Figure 18.11.

Figure 18.11 Ammonia is manufactured in this plant by the Haber process.

The key points about the manufacture of ammonia may be summarised as follows.

Ammonia is manufactured by reacting nitrogen (obtained from the air) with hydrogen (usually obtained from natural gas). The reaction may be summarised as follows:

$$N_{2\,(g)} + 3H_{2\,(g)} \overset{Fe}{\rightleftharpoons} 2NH_{3\,(g)} \quad \Delta H = -92.4 \text{ kJ mol}^{-1}$$

In words, this may be written as:

$$\text{nitrogen + hydrogen} \overset{\text{iron (catalyst)}}{\rightleftharpoons} \text{ammonia}$$

The amount of ammonia produced depends on the **temperature** and the **pressure** inside the reaction vessel.

Le Chatelier's Principle in action: Fritz Haber and Carl Bosch used Le Chatelier's Principle to figure out the best conditions for making ammonia. As seen in the above equation, there are **four moles** of reactants (on the left) and only **two moles** of ammonia (on the right), Figure 18.12. According to Le Chatelier's Principle, at **high pressure**, the equilibrium will shift to the right, producing more ammonia. By experiment, this is found to be true.

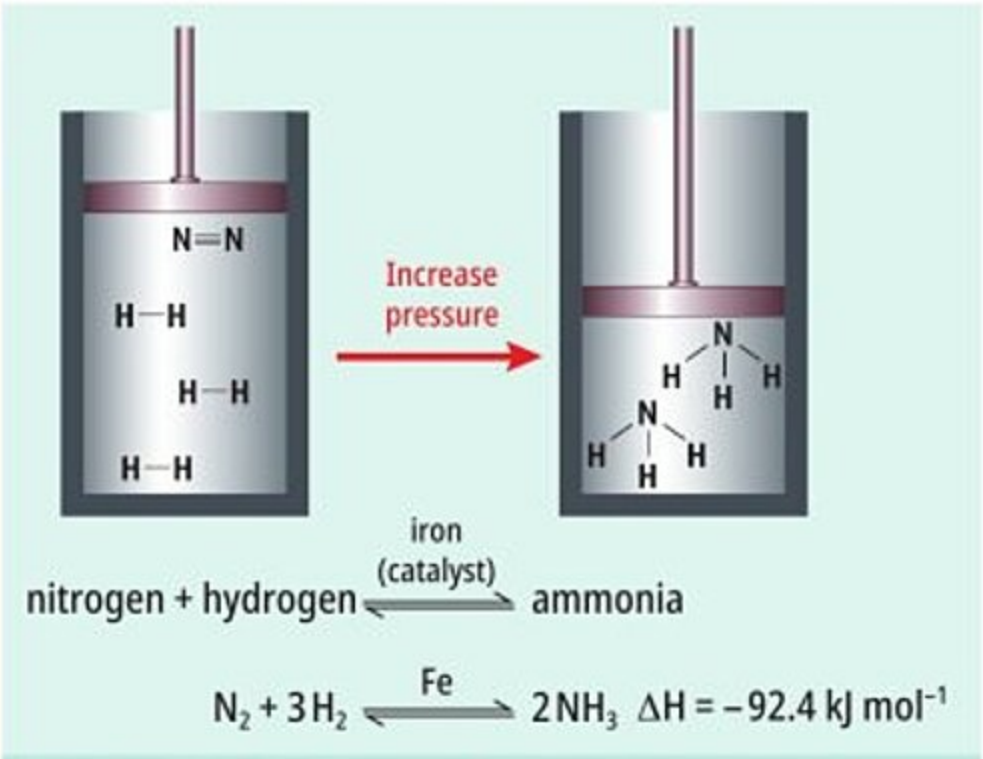


Figure 18.12 An increase in pressure causes the equilibrium to be shifted from left to right.

Pressure compromise: A high-pressure plant is expensive both to build and to maintain and the improvement in yield is not worth the extra cost. Also, with high-pressure plants there is a danger of gas leaks and other safety problems when dealing with gases under high pressure, e.g. explosions. Therefore, a **compromise pressure** of approximately **200 atmospheres** is used in the production of ammonia to ensure a relatively good yield of ammonia while also reducing the cost of a high-pressure plant.

Temperature conditions: The negative value of ΔH in the above equation tells us that the reaction is exothermic (releases heat) going from left to right. Therefore, if we lower the temperature in the reaction vessel, Le Chatelier's Principle tells us that the equilibrium will be shifted to the right, i.e. more ammonia will be produced. However, it is found that, if the temperature is too low, the rate of the reaction is too slow, i.e. the system takes a long time to come to equilibrium.

Temperature compromise: At low temperature, we would succeed in getting a high yield of ammonia (the mixture of the three gases in the reaction vessel could consist of about 90% ammonia) but the ammonia would be produced too slowly to be economically viable. Therefore, a **compromise temperature** of approximately **500 °C** is used in practice to ensure a satisfactory yield of ammonia while also ensuring that the reaction does not take too long.

In short, Le Chatelier's Principle tells us that the best conditions to maximise the yield of ammonia in the Haber process are **high pressure** and **low temperature**. However, in practice, a balance is needed between yield and reaction speed.

The Haber process involves a method of removing the ammonia as it is formed (thus pushing the equilibrium to the right) and continuously feeding in new reactants.

Role of catalysts in industrial processes

In industrial processes, catalysts make a very valuable contribution to the economy of the process. For example, in the Haber process, the percentage conversion of nitrogen and hydrogen to ammonia under the above conditions at which a typical plant operates is small. However, using a catalyst enables the same percentage conversion to be achieved in a much shorter time, i.e. it brings the system to equilibrium more quickly. In addition, it allows the reaction to be carried out at a lower temperature than would be the case if no catalyst were present. This increases the productivity of the plant and hence makes the process more economical.

TEST YOURSELF: Attempt Questions 18.1–18.2 and W18.1–W18.5.

18.5 The equilibrium constant

So far we have discussed equilibrium from a descriptive point of view. We have seen how various factors can affect the position of equilibrium and shift it to the left or to the right. When a system reaches a state of equilibrium, chemists and chemical engineers need to know the exact concentrations of reactants and products that exist in the equilibrium mixture. In some cases, it is possible to determine these concentrations by experiment. In other cases, it is necessary to determine these concentrations by performing calculations. In this section, we consider how chemists and chemical engineers perform calculations relating to systems that have reached a state of equilibrium.

By experiment, it has been discovered that, provided the temperature remains constant, there is a simple mathematical relationship between the concentrations of the reactants and products in an equilibrium mixture. This simple relationship is based on a law known as the **Law of Chemical Equilibrium** or the **Equilibrium Law**. Consider the reaction in which **a** moles of reactant A react with **b** moles of reactant B to form **c** moles of product C and **d** moles of product D at equilibrium.

$$aA + bB \rightleftharpoons cC + dD$$

It has been found by experiment that the concentrations of all species at equilibrium are related by the expression:

$$K_c = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$$

equilibrium constant

concentration in moles/litre

K_c is called the **equilibrium constant**. (The 'K' represents the constant and the subscript 'c' stands for concentration since the value of K depends on the concentrations of the reactants and products at equilibrium.) **The square brackets represent concentration measured in moles per litre**.

It is very important for you to be able to write correct equilibrium constant expressions when given the balanced equation.

Note the following points carefully:

- The products are always written above the line (in the numerator) and the reactants are always written below the line (in the denominator).
- The concentrations of the products are multiplied together. The concentrations of the reactants are multiplied together. The multiplication sign is usually omitted.
- The concentration of each species is raised to the power of its coefficient in the balanced equation.
- Thus, the equilibrium constant expression for the reaction:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$$

is $$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

Every equilibrium reaction has its own value for K_c at the particular temperature at which the reaction takes place. For example, at 458 °C the value of K_c for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ is 46 (approximately).

By experiment it is found that this K_c value of 46 is always obtained no matter what concentrations of hydrogen and iodine are put into the container and allowed to reach equilibrium at that temperature, Figure 18.13.

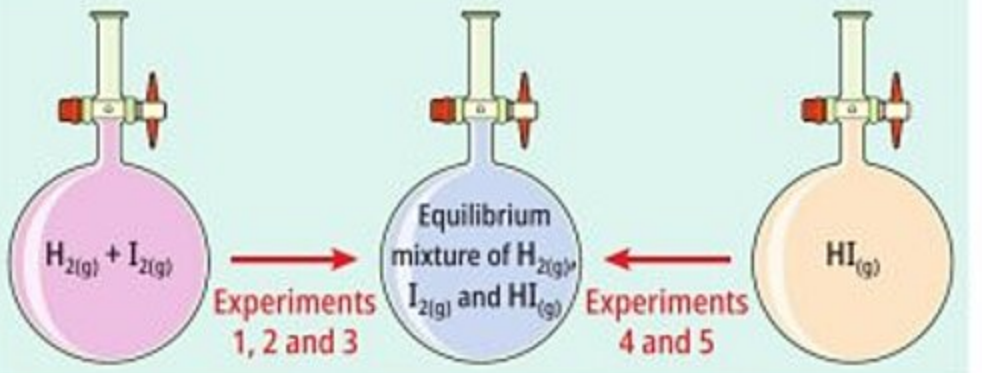


Figure 18.13 The equilibrium $H_2 + I_2 \rightleftharpoons 2HI$ can be set up starting either with a mixture of hydrogen and iodine or with hydrogen iodide on its own in the container.

Instead of putting hydrogen and iodine into the container, you could inject hydrogen iodide gas into the container and let it stand until equilibrium is reached. You could then determine the equilibrium concentrations of each of the three gases in the mixture by experiment. The results from five such experiments are given in Table 18.1. Note that a similar value for K_c is obtained in each case.

Expt. No.	Initial concentrations (moles/litre)			Equilibrium concentrations (moles/litre)			
	$[H_2] \times 10^{-2}$	$[I_2] \times 10^{-2}$	$[HI] \times 10^{-2}$	$[H_2] \times 10^{-2}$	$[I_2] \times 10^{-2}$	$[HI] \times 10^{-2}$	$K_c = \frac{[HI]^2}{[H_2][I_2]}$
1	2.4	1.38	0	1.14	0.12	2.52	46.4
2	2.44	1.98	0	0.77	0.31	3.34	46.7
3	2.46	1.76	0	0.92	0.22	3.08	46.9
4	0	0	3.04	0.345	0.345	2.35	46.4
5	0	0	7.58	0.86	0.86	5.86	46.4

Table 18.1 The results of five experiments carried out to determine the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$

Some important points about K_c may be summarised as follows:

- In the above example, the value of 46 for K_c tells us that the numerator is much greater than the denominator, i.e. the concentration of the product is much greater than that of the reactants. The value for K_c gives us an idea of how far the equilibrium is pushed to the right, i.e. how far a reaction goes to completion. **The larger the value of K_c, the greater is the extent to which the equilibrium is pushed towards the products**. A low value of K_c tells us that only a small fraction of the reactants has been converted to products.
- In the preceding sections, we have used the term *position of equilibrium* to describe equilibrium reactions. When we say that the position of equilibrium lies on the right-hand side of the equation, this means that the reaction has a large equilibrium constant. If the equilibrium lies on the left of the equation, the reaction has a small equilibrium constant.
- You may find it helpful to think of the equilibrium constant K_c as a measure of the ratio between products and reactants when a reaction reaches equilibrium. If K_c has a high value, this means that the side of the products is favoured. If K_c has a low value, this means that the side of the reactants is favoured.

Temperature: The only factor affecting the value of K_c

Whenever a value of K_c for a particular reaction is quoted, the temperature is usually stated. This is because the value of K_c depends on temperature. In fact, temperature is the only factor that affects the value of K_c. Changing the temperature shifts the equilibrium in a particular direction.

Think of the equilibrium constant K_c as a measure of the balance between products and reactants when a reaction reaches equilibrium. If K_c has a high value, this means that the side of products is favoured. If K_c is low, this means that the side of reactants is favoured.

A change in temperature determines whether the equilibrium reaction is pushed in the forward or backward direction.

- If the forward reaction is **endothermic**, then raising the temperature will push the reaction in the forward direction (to absorb the added heat). This produces more products and, therefore, the value of K_c will increase. If the temperature is lowered, this will push the reaction in the backward direction (to produce more heat). This decreases the concentration of products and, therefore, the value of K_c will decrease.
- If the forward reaction is **exothermic**, then raising the temperature will push the reaction in the backward direction (to absorb the added heat). This decreases the concentration of products and, therefore, the value of K_c will decrease. If the temperature is lowered, this will push the reaction in the forward direction (to produce more heat). This increases the concentration of products and, therefore, the value of K_c will increase.

For example, consider the reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

For this reaction at 127 °C, K_c has a value of 4390. At 327 °C, K_c has a value of 4.03. At 527 °C, K_c has a value of 0.03.

Why does a change in concentration of reactants and products not affect the value of K_c?

- Changing the concentrations of reactants or products only shifts the position of the equilibrium to either favour the reactants or the products and re-establish equilibrium (Le Chatelier's Principle). For example: If you add more reactants, the system will shift toward producing more products until the original ratio of concentrations is restored. Conversely, if you add more products, the reaction shifts to produce more reactants until the original ratio of concentrations is restored.
- Even though the concentrations of individual reactants and products may increase or decrease as the reaction shifts, their ratio at equilibrium remains the same. This means that the equilibrium constant K_c does not change.
- In short, K_c is not affected by **the starting amounts** of reactants or products because the value of K_c depends on the concentrations at equilibrium – not the specific concentrations at any given time before equilibrium is re-established.

As shown in Table 18.1, at constant temperature, a new state of equilibrium is always reached with the same approximate value of K_c.

Why does a change in pressure (for gaseous reactions) not affect the value of K_c?

Changing pressure affects the position of equilibrium in reactions involving gases with unequal number of moles on either side of the equation. The equilibrium will shift to accommodate the change and re-establish equilibrium. This shift in equilibrium due to pressure change helps to counteract the pressure change and re-establish equilibrium. However, it does not change the **ratio** of the concentrations of reactants and products at equilibrium. Therefore, the value of K_c will be unchanged.

Why does a catalyst have no effect on the value of K_c?

- A catalyst helps a reaction to reach equilibrium more quickly, i.e. a catalyst only affects the rate of a reaction by speeding up the time taken to reach equilibrium.
- A catalyst alters the rate of the forward and backward reactions equally. In other words, in the presence of a catalyst, the products are produced and used up at the same rate. Therefore, a catalyst does not change the overall ratio of concentrations of products to reactants at equilibrium.
- In short, a catalyst has no effect on the composition of the equilibrium mixture. Therefore, a catalyst has no effect on the value of the equilibrium constant K_c.

EXAM TIP!

In an exam, it is always helpful to state that K_c is only affected by temperature.

How do I work out the units of K_c?

The units of K_c depend on the reaction itself. For example in the reaction:

$$H_2 + I_2 \rightleftharpoons 2HI$$

The units of K_c can be found by proceeding as follows:

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(\text{moles/L})^2}{(\text{moles/L})(\text{moles/L})}$$

Since the units cancel out, there are no units for K_c in this particular case.

However, for the reaction:

$$N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3(g)}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$K_c = \frac{(\text{moles/L})^2}{(\text{moles/L})(\text{moles/L})^3}$$

$$K_c = \frac{1}{(\text{moles/L})^2}$$

Therefore, the units in this case are $(\text{moles/L})^{-2}$.

When stating a value for K_c it is essential to give the equation to which it refers. For example, we have already seen that at 458 °C, the value of K_c for the equilibrium $H_2 + I_2 \rightleftharpoons 2HI$ is 46 approx.

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = 46$$

However, if we write the equilibrium reaction as $2HI \rightleftharpoons H_2 + I_2$ then the new K_c (represented as K'_c) will be:

$$K'_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{1}{46}$$

If the equilibrium reaction is written as $\frac{1}{2}H_2 + \frac{1}{2}I_2 \rightleftharpoons HI$, then a different value of K (represented as K''_c) will be obtained.

$$K''_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = \sqrt{46}$$

While the value of the equilibrium constant gives us information about the extent of a reaction, it tells us nothing about the rate of a reaction. In other words, K_c tells us how **far** a reaction has gone but not how **fast** the reaction goes.

Example 18.2

Question

Phosphorus(V) chloride decomposes into phosphorus(III) chloride and chlorine at a temperature of 500 K according to the following balanced equation.

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

(a) When the temperature of the equilibrium mixture is increased, the phosphorus(V) chloride decomposes further. Is the reaction endothermic or exothermic? Justify your answer.

(b) What changes, if any, would an increase in pressure have on the value of K_c? Explain. [LCH]

Answer

(a) The forward reaction is endothermic. The reason for this is that the system responds to absorb the heat added. Since the PCl_5 decomposes further, this means that the forward reaction absorbs heat, i.e. the forward reaction must be endothermic.

(b) The increase in pressure will have no effect on K_c.

The reason for this is that the value of K_c is always constant at constant temperature.

18.6 Calculations using the Law of Chemical Equilibrium

Chemists and chemical engineers make great use of the Law of Chemical Equilibrium to deduce information about systems that have reached a state of equilibrium. The following examples demonstrate some of these uses.

(a) To calculate the value of K_c given equilibrium concentrations

Example 18.3

Question

The reaction:

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

was allowed to reach equilibrium at 450 °C in a one litre container. It was found that there were 13.6 moles N_2, 1.0 mole H_2 and 1.5 moles NH_3 in the container when equilibrium had been established. Calculate the value of K_c at this temperature.

Answer

To solve this problem simply write the equilibrium constant expression for the reaction and substitute in the appropriate values. Since we are told that the container is one litre, then the concentrations given are automatically in moles per litre.

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(1.5)^2}{(13.6)(1.0)^3} = 0.165$$

Answer: $K_c = 0.165$

» Study Example 18.4 in the online resources.

Example 18.5

Question

The thermal decomposition of phosphorus pentachloride is represented by the following equation:

$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$

A mass of 20.85 g of phosphorus pentachloride was heated at 523 K in a closed 8-litre vessel. When the reaction had come to equilibrium at that temperature, it was found that 80% of the pentachloride had dissociated.

(i) What is meant by chemical equilibrium? Why is it described as a dynamic process?

(ii) What would be the effect, if any, on the percentage decomposition of the phosphorus pentachloride if the reaction were carried out at a higher pressure?

(iii) Calculate K_c for the reaction. [LCH]

Answer

(i) Chemical equilibrium is a state of dynamic balance where the rate of the forward reaction equals the rate of the reverse reaction.

It is described as a dynamic process because both the forward and reverse reactions are still taking place even though the overall reaction seems to have stopped.

(ii) Less PCl_5 would have dissociated since, according to Le Chatelier's Principle, at higher pressure the equilibrium is pushed to the left-hand side of the above equation due to the fact that there is a smaller number of moles on the left-hand side of the equation.

(iii) No. of moles of $PCl_5 = \frac{\text{Mass}}{\text{Rel. molecular mass}} = \frac{20.85}{208.22} = 0.100$

Since 80% of PCl_5 dissociates, then the number of moles of PCl_3 and Cl_2 will be 80% of 0.1 mole i.e. 0.08 mole.

	$PCl_{5(g)}$	$\rightleftharpoons$	$PCl_{3(g)}$	+	$Cl_{2(g)}$
Initially	0.1		0		0
At equil.	0.1 – 0.08 = 0.02		0.08		0.08
Conc. at equil. (V = 8L)	$\frac{0.02}{8}$ = [0.0025]		$\frac{0.08}{8}$ = [0.01]		$\frac{0.08}{8}$ = [0.01]

$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

$K_c = \frac{(0.01)(0.01)}{(0.0025)} = 0.04$

Answer: $K_c = 0.04$

P	= 30.97
5 Cl = 5 x 35.45	= 177.25
M_r PCl_5	= 208.22

It is very important that you have plenty of practice in solving problems of this type. For this reason, it is strongly recommended that you work through the questions at the end of this chapter and in the *Assessment and Exam Guide*.

(b) To calculate the equilibrium concentrations given the value of K_c

» Study Example 18.6 in the online resources.

SEC exam question 18.7

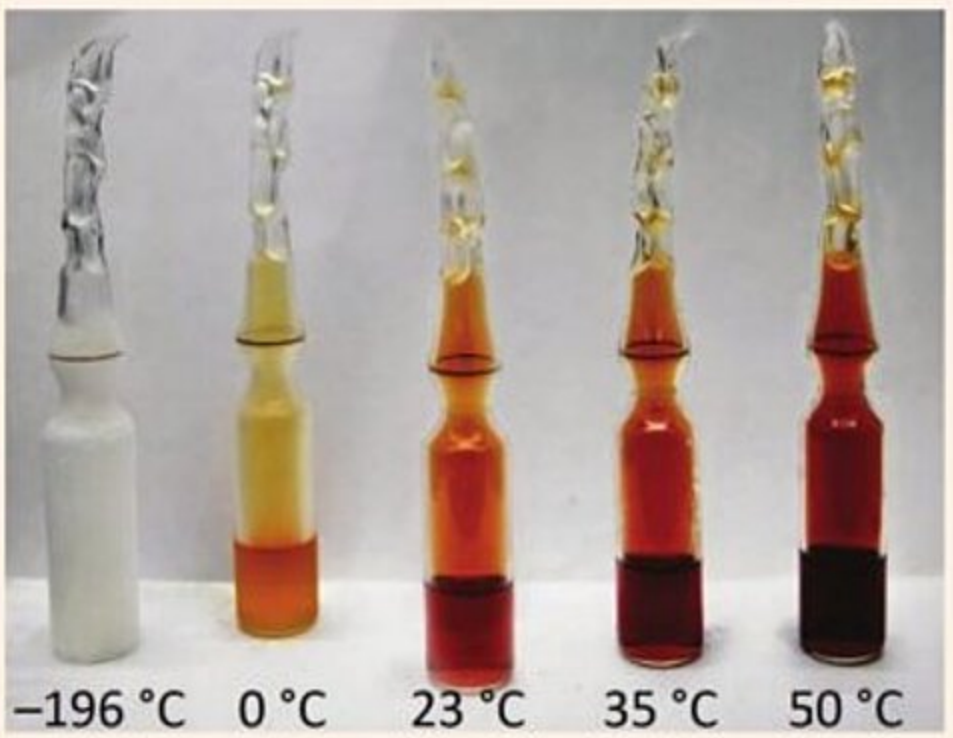
Question

An oxide of nitrogen is nitrogen dioxide (NO_2), a brown compound which forms an equilibrium mixture with colourless dinitrogen tetroxide (N_2O_4), as described by the following balanced chemical equation:

$$2NO_2 \rightleftharpoons N_2O_4$$

brown colourless

The photograph shows the equilibrium mixture at five different temperatures.



Question

(i) Is the conversion of NO_2 to N_2O_4 (the forward reaction) exothermic or endothermic? Justify your answer.

Answer

The forward reaction is exothermic.

- As the temperature increases, the brown colour gets darker.
- Therefore, there is more NO_2 and less N_2O_4 at higher temperature.
- Therefore, the increase in temperature favours the backward reaction.
- Therefore, the backward reaction must be endothermic since according to Le Chatelier's Principle, the equilibrium is shifted in such a way that the added heat is absorbed.
- Therefore the forward reaction must be exothermic.

Question

$K_c = 0.5$ for this reaction at temperature *T*.

When 2 moles of pure NO_2 and 1 mole of pure N_2O_4 were sealed in a 1 litre vessel, a reaction occurred and an equilibrium was established at temperature *T*.

(ii) Calculate the number of moles of each gas present when the reaction is at equilibrium.

Answer

Step 1

Write out the concentrations:

	$2NO_2$	$\rightleftharpoons$	N_2O_4
Initially	[2]		[1]
At equilibrium	2 - 2x		1+x
Conc. at equil (V= 1)	[2 - 2x]		[1 +x]

x = no of moles of NO_2 that react.

Step 2

Input data into equilibrium expression.

$$K_c = \frac{[N_2O_4]}{[NO_2]^2}$$

$$0.5 = \frac{1 + x}{(2 - 2x)^2}$$

Step 3

Solve for x.

$$0.5 = \frac{1 + x}{4 - 8x + 4x^2}$$

$$0.5\,(4 - 8x + 4x^2) = 1 + x$$

$$2 - 4x + 2x^2 = 1 + x$$

$$2 - 1 - 4x - x + 2x^2 = 0$$

$$2x^2 - 5x + 1 = 0$$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$x = 2.28$ or $x = 0.219$

Step 4

Determine which x is chemically possible.

For x = 2.28: this is not possible as we started with only 2 moles NO_2.

For x = 0.22:

$[NO_2]$: = 2 – 2x = 2 – 2(0.22) = 1.56 mol/L

$[N_2O_4]$: 1 + x = 1 + 0.22 = 1.22 mol/L

Answer: NO_2 = 1.56 moles, N_2O_4 = 1.22 moles

TEST YOURSELF: Attempt Questions 18.3–18.6 and W18.6–W18.19.

Summary What I should know

- Chemical equilibrium is a state of dynamic balance where the rate of the forward reaction is the same as the rate of the backward reaction.
- In a dynamic state, the reactants are continuously forming products and the products are continuously forming reactants.
- In a **closed system** the concentrations of reactants and products remain constant at equilibrium because no substances can enter or leave the system.
- Le Chatelier's Principle states that, if a stress is applied to a system at equilibrium, the system readjusts to relieve the stress applied.
- Le Chatelier's Principle predicts that, in an all-gaseous reaction, an increase in pressure will favour the reaction that results in a reduction in volume, i.e. it will shift the reaction towards the side with the smaller number of molecules.
- Le Chatelier's Principle predicts that the best conditions to maximise the yield of ammonia in the Haber Process are high pressure and low temperature.
- The Law of Chemical Equilibrium states that for:

  $aA + bB \rightleftharpoons cC + dD$

  $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

- The Law of Chemical Equilibrium may be used in calculations involving systems at equilibrium.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the concept of dynamic chemical equilibrium.	⬡	⬡	⬡
Use Le Chatelier's Principle to predict the direction taken by a reaction at chemical equilibrium if the conditions of the reaction are changed.	⬡	⬡	⬡
Investigate using primary data (in the laboratory) and also secondary data how changes in temperature and concentration can affect the state of equilibrium.	⬡	⬡	⬡
Solve problems to (i) calculate the value of K_c given equilibrium concentrations and (ii) calculate equilibrium concentrations given the value of K_c.	⬡	⬡	⬡

Chapter review questions

18.1 When bromine (a red liquid) is added to water, the bromine reacts with the OH^- ions in the water and the following equilibrium is established:

$$Br_2 + 2OH^- \rightleftharpoons Br^- + BrO^- + H_2O$$

red — all colourless species

All of the species on the right-hand side are colourless.

(a) Predict the direction in which the equilibrium will be shifted if some sodium hydroxide, NaOH, is added.

(b) What colour change will be observed on adding the sodium hydroxide?

(c) Suggest a way of reversing the colour change.

18.2 Hydrogen and iodine react with each other in the following reversible reaction:

$$H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$$

Samples of hydrogen gas and iodine gas were placed in a flask as shown in Figure 18.14 and allowed to reach equilibrium. In your copybook, draw a picture to represent what you would expect to find inside the flask when equilibrium is established. Assume that at equilibrium, one-third of the molecules of hydrogen and iodine have reacted to form hydrogen iodide.

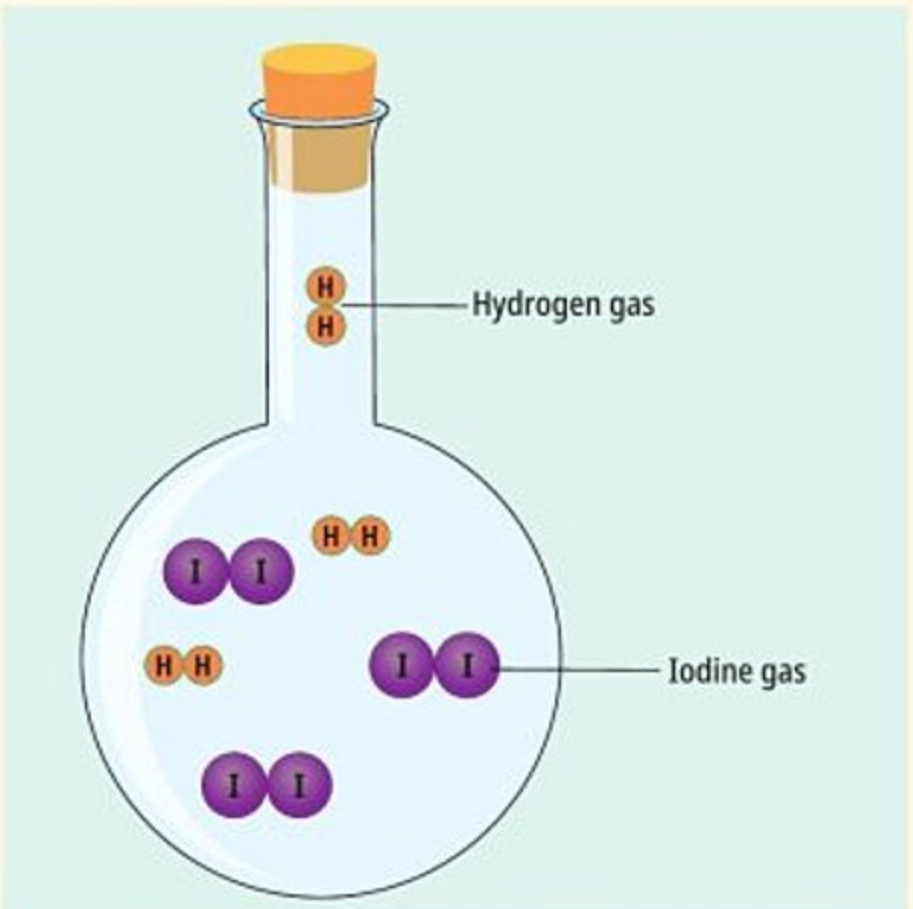


Figure 18.14

18.3 Write the expression for K_c for each of the following reactions:

(a) $2CO_{(g)} + O_{2\,(g)} \rightleftharpoons 2CO_{2\,(g)}$

(b) $C_2H_{6\,(g)} \rightleftharpoons C_2H_{4\,(g)} + H_{2\,(g)}$

(c) $NO_{2\,(g)} \rightleftharpoons \frac{1}{2} N_2O_{4\,(g)}$

(d) $CO_{(g)} + H_2O_{(g)} \rightleftharpoons CO_{2\,(g)} + H_{2\,(g)}$

18.4 One mole of ethanoic acid and one mole of ethanol were mixed in a container and allowed to reach equilibrium at 25 °C.

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

When the mixture was analysed, it was found that 0.33 moles of unreacted ethanoic acid remained while the rest reacted to form ethyl ethanoate. Calculate the value of K_c for this reaction.

18.5 One mole of hydrogen iodide was injected into a 1 litre flask at 450 °C. The following equilibrium was set up:

$$2HI \rightleftharpoons H_2 + I_2$$

It was found that 0.80 moles of HI were present at equilibrium. Calculate the value of K_c.

18.6 Bromine monochloride dissociated on heating according to the equation:

$$2BrCl \rightleftharpoons Br_2 + Cl_2$$

In an experiment, 0.9 mole of BrCl was heated in a 5 litre vessel at a certain temperature until equilibrium was established. The amount of free chlorine in the mixture was found to be 0.4 moles.

(i) Write the equilibrium constant expression for this reaction.

(ii) Calculate the value of the equilibrium constant for the reaction at this temperature.

(iii) Explain why it is not necessary to know the volume of the vessel in calculating the equilibrium constant.

(iv) Is the value of the equilibrium constant for the reaction when represented by the equation $BrCl \rightleftharpoons \frac{1}{2} Br_2 + \frac{1}{2} Cl_2$ the same as that calculated in (ii) above? Explain your answer. [LCH]

19 pH and Indicators

19.1 Introduction

In Chapter 11, we learned about some of the properties of acids and bases. We saw that an acid could be described as a substance that donates protons. A base was described as a substance that accepts protons. In this chapter, we will consider the strengths of acids and bases and the effect of adding acids and bases to water. We will then look at how chemists measure the levels of acidity in water, and finally we will study how acid–base indicators work.

OBJECTIVES

- To give students an understanding of the concept of pH.
- To make students familiar with strengths of acids and bases.
- To provide students with the opportunity to carry out pH calculations.
- To make students familiar with drawing and interpreting pH titration curves.

19.2 Self-ionisation of water

Chemists discovered that even pure water will conduct a tiny electric current. If the water is pure, how do we explain that there are ions present to carry the electric current? The presence of these ions is explained by the fact that water is a substance that dissociates slightly to form ions:

$$H_2O \rightleftharpoons H^+ + OH^-$$

The above occurrence is often referred to as the **self-ionisation of water**. The self-ionisation of water may also be represented by the equation:

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

The concentration of H^+ and OH^- ions in pure water is extremely small, i.e. the equilibrium lies very much on the left-hand side of the above equations. The equilibrium constant expression for the above reaction may be written as:

$$K_c = \frac{[H^+][OH^-]}{[H_2O]}$$

In the above expression, the actual value of the $[H_2O]$ term is easily calculated, i.e. the concentration of water in moles per litre. The density of water is 1 g/cm^3. Therefore, a litre of water (1000 cm^3) has a mass of 1000 g.

No. of moles of water in a litre of water

$$= \frac{\text{Mass}}{\text{Rel. molecular mass}} = \frac{1000}{18} = 55.56 \text{ moles}$$

Since any variation in the term $[H_2O]$ is extremely small in relation to its size, it may be taken to have a constant value. Therefore, the above equation can be rearranged to give:

$$K_c[H_2O] = [H^+][OH^-]$$

The two terms on the left-hand side of the above equation are both constants. Therefore, these two constants can be replaced by a new constant indicated by the symbol K_w.

$$K_w = K_c[H_2O] = [H^+][OH^-]$$

ionic product of water

This new constant, K_w, is given a special name. As it is calculated by multiplying together the concentrations (in moles per litre) of the H^+ and OH^- ions in water, it is called the **ionic product of water**.

The value of K_w has been measured experimentally and, at 25 °C, has been found to be 1×10^{-14}. (The units are moles^2/litre^2 but these need not concern us in this course.) Note that the value is temperature-dependent, as is the case with all equilibrium constants, Table 19.1.

Temp (°C)	K_w
0	0.11×10^{-14}
10	0.30×10^{-14}
20	0.68×10^{-14}
25	1.01×10^{-14}
30	1.47×10^{-14}
40	2.92×10^{-14}
50	5.48×10^{-14}
60	9.61×10^{-14}
70	16.2×10^{-14}
80	24.7×10^{-14}
90	36.0×10^{-14}
100	51.3×10^{-14}

Table 19.1 The ionic product of water varies with temperature.

Why is the ionic product of water temperature dependent?

Let's take a closer look at the dissociation of water.

$$H_2O \rightleftharpoons H^+ + OH^- \qquad \Delta H = +55.8 \text{ kJ mol}^{-1}$$

- Note that the forward reaction is endothermic.
- When you increase the temperature, then according to Le Chatelier's Principle, the equilibrium will shift from left to right to absorb the added heat.
- Therefore more H^+ ions and more OH^- ions are produced.
- Therefore K_w increases, Figure 19.0.

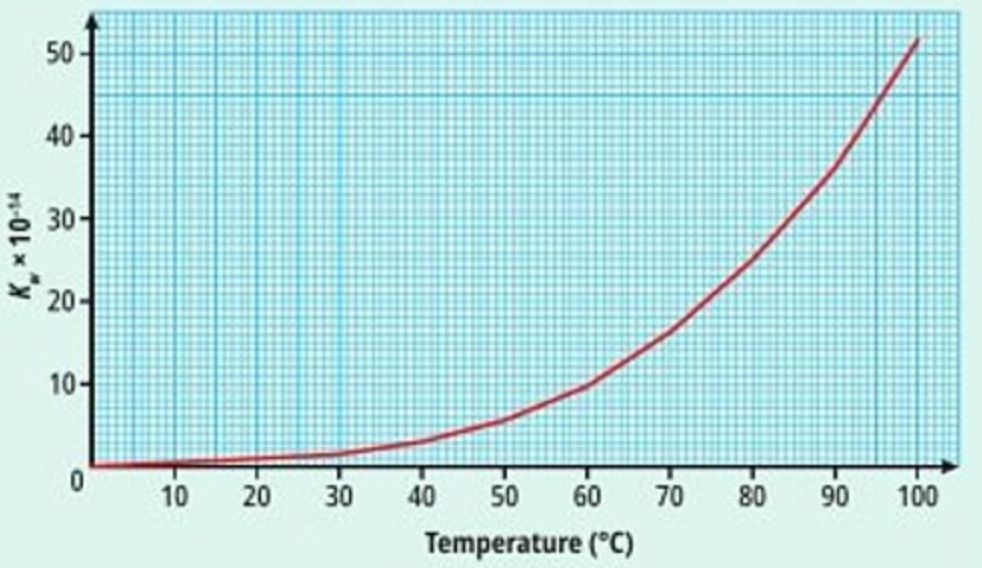


Figure 19.0 As the temperature increases, note that the value of K_w increases.

Note from the graph:

- The value of the ionic product of water depends on temperature.
- As the temperature is increased, the value of the ionic product of water also increases.

Calculating the concentration of H^+ ions in pure water

Let us now calculate the actual concentration of H^+ ions in pure water.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Since $[H^+] = [OH^-]$ then $[H^+]^2 = 1.0 \times 10^{-14}$

Therefore, $[H^+] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}$

and $[OH^-] = 1.0 \times 10^{-7}$

In other words, for a **neutral solution** at 25 °C:

$$[H^+] = [OH^-] = 1.0 \times 10^{-7}$$

Now consider what happens when an acid (e.g. HCl) is added to the water. The acid increases the concentration of H^+ ions. However, since K_w is a constant, the value of K_w cannot change.

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Therefore, if the value of $[H^+]$ increases (to say 10^{-5}), the value of $[OH^-]$ must decrease (to say 10^{-9}) so that the two values multiplied together will equal 1.0×10^{-14}.

In other words, for an **acidic solution**:

$$[H^+] > [OH^-]$$

e.g. $(10^{-5}) > (10^{-9})$

Now consider what happens when a base (e.g. NaOH) is added to water. The base increases the concentration of OH^- ions. However, since the value of K_w is a constant, then the value of $[H^+]$ must decrease in order to satisfy the equation:

$$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$$

Therefore, if the value of $[OH^-]$ increases (to say 10^{-6}), the value of $[H^+]$ must decrease (to say 10^{-8}) so that the two values multiplied together will equal 1.0×10^{-14}.

In other words, for a **basic solution**:

$$[H^+] < [OH^-]$$

e.g. $(10^{-8}) < (10^{-6})$

The relationship of $[H^+]$ to levels of acidity and basicity at 25 °C may be summarised as shown in Figure 19.1.

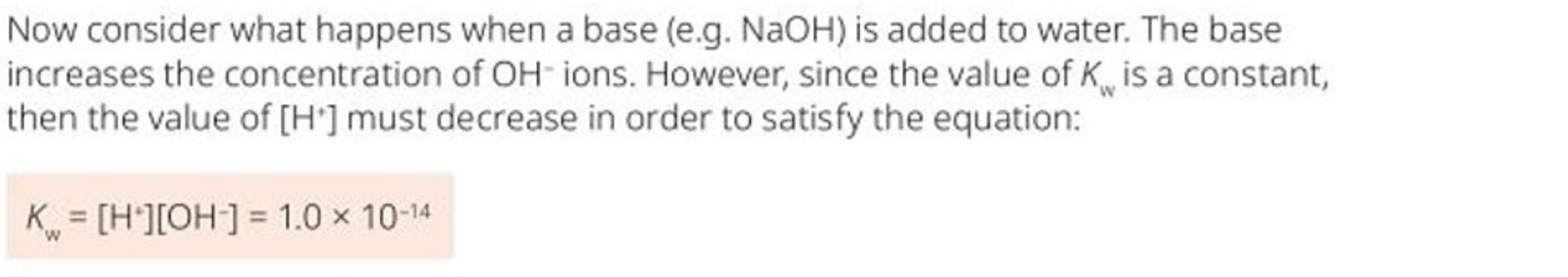


Figure 19.1 If $[H^+] > 10^{-7}$, the solution is acidic. If $[H^+] < 10^{-7}$, the solution is basic. If $[H^+] = 10^{-7}$, the solution is neutral. All concentrations are measured in moles per litre.

19.3 Measurement of acidity: The pH scale

You will have discovered when reading the previous page that expressing concentrations of solutions in terms of hydrogen ion concentrations is a bit confusing! Chemists don't like having to use numbers like 10^{-7} to express the concentrations of hydrogen ions in solution. It was for this reason that in 1909 a Danish chemist called Søren Sørensen devised an easier method to express the degree of acidity of a solution, Figure 19.2.

Figure 19.2
Søren Sørensen
(1868–1939)

Søren Sørensen was born in Copenhagen, Denmark. He studied chemistry at the University of Copenhagen. In 1909 he became famous when he suggested a system for making it easier to write the concentrations of hydrogen ions in solution. The pH system that he introduced is now one of the fundamental concepts in chemistry.

- Sørensen was working for a Danish brewery and decided to introduce a simpler method of reporting levels of acidity in beer.
- Instead of reporting that a solution contains 0.00001 (or 10^{-5}) moles of H^+ ions per litre, he referred to the solution as 'having a pH of 5'.
- To do this, he had to get rid of the power in the expression 10^{-5} and also to get rid of the negative sign in the power.

Therefore, he defined pH as follows:

$pH = -\log_{10}[H^+]$ where the square brackets indicate concentration in moles per litre.

The above definition of pH may also be stated in words as follows:

The **pH of a solution** is the negative logarithm to the base 10 of the hydrogen ion concentration measured in moles per litre.

- The 'p' in pH stands for 'power' and the 'H' in pH refers to the H^+ ion. Thus, pH may be roughly translated as 'power of hydrogen ions'.
- The log to the base 10 in the above definition of pH ensures that the powers of ten do not appear in the pH scale. The negative sign in the above definition of pH ensures that all pH values are positive.

Example 19.1

Question

A solution has a concentration of 10^{-4} moles of H^+ ions per litre. What is the pH of this solution?

Answer

$pH = -\log_{10}[H^+] = -\log_{10}(10^{-4}) = -(-4) = +4$ Answer: pH = 4

Studying Table 19.2 may help you to see the relationship between concentration in moles/litre of H^+ ions and pH.

Solution	$[H^+]$	pH
A	$0.001 = 1 \times 10^{-3}$	3
B	$0.000001 = 1 \times 10^{-6}$	6
C	$0.0000001 = 1 \times 10^{-7}$	7
D	$0.000000001 = 1 \times 10^{-9}$	9
E	$0.000000000001 = 1 \times 10^{-12}$	12

Table 19.2 Note that a pH value is simply the number in the power with the negative sign changed to a positive sign.

From Table 19.2 we see that solution A has the highest concentration of H^+ ions and the lowest pH. Solution E has the lowest concentration of H^+ ions and the highest pH. Studying Figure 19.3 may help you to understand this.

Figure 19.3a A low pH indicates a high concentration of H^+ ions.

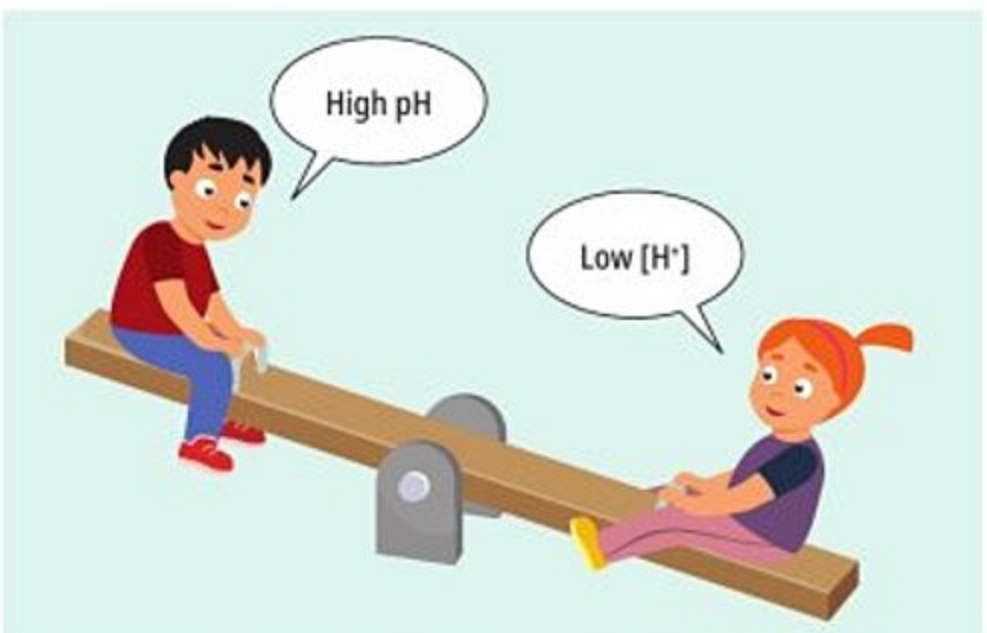


Figure 19.3b A high pH indicates a low concentration of H^+ ions.

Solution C has the same concentration of H^+ ions as pure water. Thus, a pH of 7 indicates a neutral solution at 25 °C. The relationship between concentration in moles of H^+ ions per litre and pH is summarised in Figure 19.4.

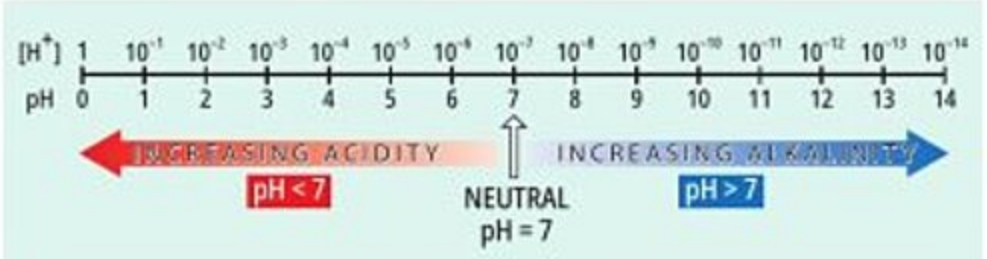


Figure 19.4 The concentration of H^+ ions in solution (measured in moles per litre) and the corresponding pH values

Note from Figure 19.4 that, as the concentration of H^+ ions increases, the pH value decreases. Also, as the concentration of H^+ ions decreases, the pH value increases.

Therefore, at 25 °C, we can say that:

The pH of an acidic solution is less than 7.
The pH of a basic (alkaline) solution is greater than 7.
The pH of a neutral solution is equal to 7.

Note: In all subsequent calculations involving pH, you will be using a scientific calculator. Make sure you know how to use it to enter powers, obtain logs, and obtain antilogs.

Example 19.2

Question

Calculate the pH of a solution whose hydrogen ion concentration is 7.1×10^{-7} mol/L.

Answer

$pH = -\log_{10}[H^+] = -\log_{10}(7.1 \times 10^{-7}) = 6.15$

Answer: pH = 6.15

Example 19.3

Question

Calculate the hydrogen ion concentration (in moles per litre) of a solution whose pH is 3.7.

Answer

$pH = -\log_{10}[H^+] = 3.7$

$\log_{10}[H^+] = -3.7$

$[H^+] = \text{antilog}(-3.7) = 1.995 \times 10^{-4}$

Answer: $[H^+] = 1.995 \times 10^{-4}$ mol/L

The temperature dependence of K_w

If you examine Table 19.1, you will observe that the value of K_w increases with increasing temperature. This must mean that the self-ionisation of water is endothermic, since it is favoured by higher temperatures:

$$H_2O \underset{\text{exothermic}}{\overset{\text{endothermic}}{\rightleftharpoons}} H^+ + OH^-$$

- Since the forward reaction is favoured as the temperature is increased, more hydrogen ions and hydroxide ions will be formed.
- Therefore, the value of K_w increases and the pH of pure water decreases as the temperature increases, Table 19.3. This is also illustrated in Figure 19.5.
- Since the pH decreases as temperature is increased, you might think that water would become more acidic at higher temperatures.
- However, this is not found to be the case in practice. A solution is acidic if there is an excess of hydrogen ions compared to hydroxide ions.
- **In the case of pure water, there is always the same number of hydrogen ions as hydroxide ions present.** This is because, for every H^+ ion that is formed when a molecule of H_2O dissociates, an OH^- ion is also formed.
- Therefore, pure water is always neutral regardless of its temperature, since the H^+ and OH^- ions are always present in equal concentrations.
- Always remember that the neutral value for pH is calculated from K_w. Therefore, if K_w changes, then the neutral value also changes.
- Since at 100 °C the pH value of pure water is 6.14, then the neutral value of the pH at 100 °C is 6.14 and not 7.

Temp (°C)	K_w	pH
0	0.11×10^{-14}	7.47
10	0.30×10^{-14}	7.27
20	0.68×10^{-14}	7.08
25	1.01×10^{-14}	7.00
30	1.47×10^{-14}	6.92
40	2.92×10^{-14}	6.77
50	5.48×10^{-14}	6.63
60	9.61×10^{-14}	6.51
70	16.2×10^{-14}	6.40
80	24.7×10^{-14}	6.30
90	36.0×10^{-14}	6.22
100	51.3×10^{-14}	6.14

Table 19.3 The pH of pure water decreases as the temperature increases.

It is possible to measure the pH of a substance by a number of methods. One method that you may have come across at Junior Cycle level is to use universal indicator paper, i.e. paper that turns a different colour depending on the pH of the solution into which it is dipped, Figure 19.6. Universal indicator solution may also be used.

The colour of the paper or solution is then matched against a chart of colours supplied with the indicator. We will be studying indicators in more detail in section 19.7.

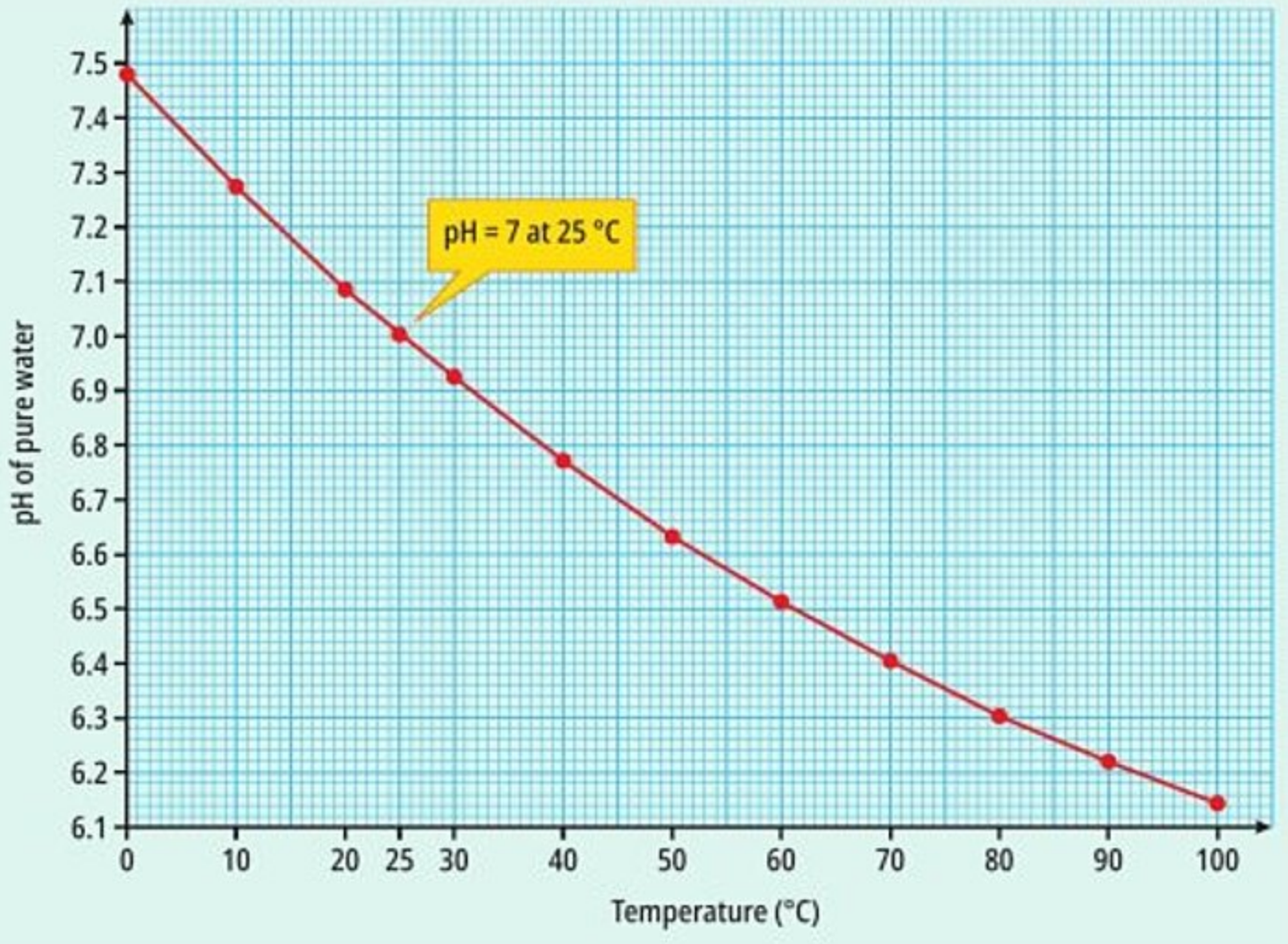


Figure 19.5 The pH of pure water decreases as the temperature increases.

Figure 19.6 Universal indicator paper or solution may be used to determine the pH of a solution.

Measuring pH using pH sensors and dataloggers

A modern method of measuring pH is to use a pH sensor and datalogger, Figure 19.7. Prior to the development of modern pH sensors and datalogging technology, instruments called pH meters were used. However, pH meters are rarely used now.

The pH sensor is sensitive to the concentration of H^+ ions in solution. The pH sensor is placed in the solution whose pH is to be measured and the pH is then read off directly on a computer or mobile phone. The pH values of some common substances are shown in Figure 19.8.

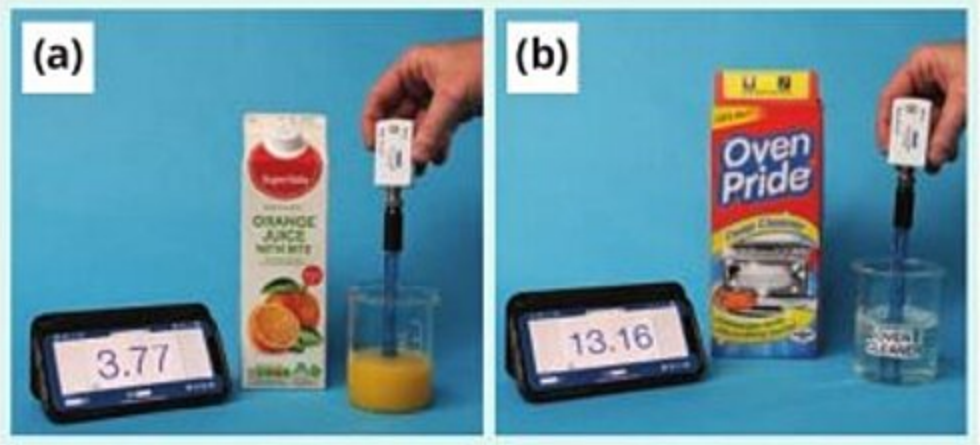


Figure 19.7 The pH of (a) the orange juice and (b) oven cleaner is being measured using a wireless pH sensor and datalogging software.

19.4 Strengths of acids and bases

In Chapter 11, we defined an acid as a proton donor. We learned that different acids donate protons to different extents. Using the Brønsted–Lowry theory, we defined a strong acid as follows:

A **strong acid** is a good proton donor, i.e. it is almost completed dissociated in water.

Acids such as HCl, H_2SO_4 and HNO_3 are classified as strong acids because they are good proton donors, i.e. they are almost completely dissociated in water.

$$HCl + H_2O \rightarrow H_3O^+ + Cl^-$$

Note that the equilibrium arrow ⇌ is not used for this equation since the reaction goes almost completely from left to right. (By experiment it is found that there is about 99.996% dissociation.)

You may recall that in Chapter 11 we learned that many acids are described as weak acids and we defined a weak acid as follows:

A **weak acid** is a poor proton donor, i.e. it does not fully dissociate in water.

Weak acids have a small tendency to donate protons, e.g. when ethanoic acid (acetic acid) is added to water, it does not fully dissociate in the water. In fact only about 1.3% of the ethanoic acid molecules are dissociated in a 0.1 M solution and the following equilibrium is set up:

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

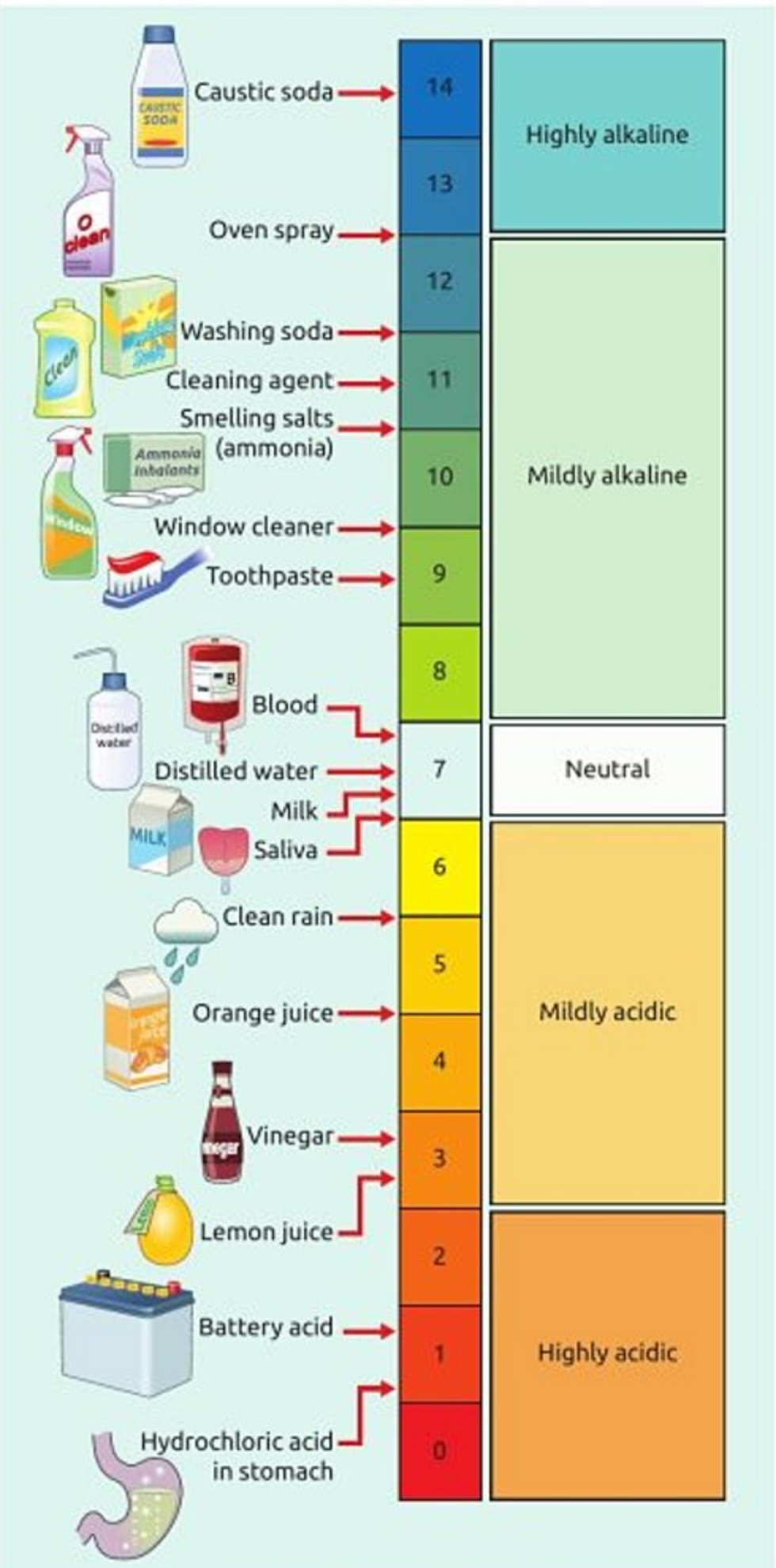


Figure 19.8 The approximate pH values of some common substances

TEST YOURSELF: Attempt Questions 19.1–19.3 and W19.1–W19.3.

Acid dissociation constant

In order to represent the strength of an acid, chemists use the symbol K_a which is known as the **acid dissociation constant**. For the general case of an acid HA undergoing dissociation:

$$HA \rightleftharpoons H^+ + A^-$$

The acid dissociation constant, K_a, is defined as:

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Sometimes, the formation of the hydronium ion, H_3O^+, is shown in the equilibrium reaction.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

In this case, K_a is written as:

$$K_a = \frac{[H_3O^+][A^-]}{[H_A]}$$

- Note that $[H_2O]$ does not appear in the K_a expression. This is because K_a is defined purely in terms of the dissociation of the acid. (The $[H_2O]$ would be included if you were simply asked to write K_c for the reaction.)
- Acid dissociation constants derive from equilibrium constants for particular acids by assuming that $[H_2O]$ is constant.
- Acid dissociation constants are constant for each particular acid and only vary with temperature. Remember this point about varying with temperature, as we will come back to it again later on in this chapter.
- The value of K_a gives us an accurate measure of the extent to which an acid is dissociated. In other words, it tells us how strong the acid is. For example, for an acid such as hydrochloric acid, which is almost completely dissociated in water, the value of K_a is very large. This is because, for a strong acid, the concentrations of H^+ ions and A^- ions in solution are very large.
- On the other hand, for a weak acid such as ethanoic acid, little dissociation occurs and therefore the concentrations of H^+ and A^- ions are small. Therefore, the value of K_a is small.

The values of K_a for some acids are listed in Table 19.4.

Name of acid	Type of acid	Formula	K_a
Hydrochloric acid	Strong acid	HCl	1×10^7
Nitric acid	Strong acid	HNO_3	1×10^5
Sulfuric acid	Strong acid	H_2SO_4	1×10^3
Hydrofluoric Acid	Weak acid	HF	6.6×10^{-4}
Methanoic acid	Weak acid	HCOOH	1.8×10^{-4}
Ethanoic acid	Weak acid	CH_3COOH	1.8×10^{-5}
Benzoic acid	Weak acid	C_6H_5COOH	6.3×10^{-5}

Table 19.4 The dissociation constants of some acids at 25 °C. The value of K_a provides an accurate measure of the extent to which an acid dissociates, i.e. the strength of that acid.

- Strong acids have relatively large values of K_a.
- Weak acids have small values of K_a.
- As a general rule, if the value of K_a is less than 10^{-2}, the acid is classified as a weak acid.

The larger the value of K_a, the higher is the concentration of H_3O^+ and the stronger is the acid.

Acid dissociation constants allow us to compare the relative strengths of different acids. For example, in the case of ethanoic acid (CH_3COOH) at 25 °C:

$$K_a = \frac{[H_3O^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5}$$

Similarly, in the case of hydrofluoric acid (HF) at 25 °C:

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} = 6.6 \times 10^{-4}$$

Since K_a for hydrofluoric acid is greater than that of ethanoic acid, we conclude that HF is a stronger acid than CH_3COOH.

In Chapter 11, we learned about strong bases and weak bases. We defined a strong base as follows:

A **strong base** is a good proton acceptor.

Sodium hydroxide (NaOH) and potassium hydroxide (KOH) are examples of strong bases, since they accept protons readily.

e.g. $NaOH + HCl \rightarrow NaCl + H_2O$

The equilibrium arrow is not used for this equation, since the reaction goes almost completely from left to right, as NaOH is a good proton acceptor.

We also learned in Chapter 11 that a weak base is defined as follows:

A **weak base** is a poor proton acceptor.

For a weak base, we can write the dissociation as follows:

$$BOH \rightleftharpoons B^+ + OH^-$$

In this case, K_b, the base dissociation constant, is written as:

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

For example, magnesium hydroxide is a weak base that is slightly soluble in water and dissociates in water as follows:

$$Mg(OH)_2 \rightleftharpoons Mg^{2+} + 2OH^-$$

$$K_b = \frac{[Mg^{2+}][OH^-]^2}{[Mg(OH)_2]}$$

The most common weak base that we will meet in this course is ammonia, NH_3. The reaction of ammonia with water may be written as:

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$$

Since the ammonia molecule has a poor tendency to accept a proton, the equilibrium lies on the left-hand side. The value of K_b, the base dissociation constant, gives an indication of the degree of dissociation.

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

The value of K_b for ammonia is only 1.74×10^{-5}. This confirms that ammonia is a weak base. The values of K_b for some bases are listed in Table 19.5.

Name of base	Type of base	Formula	K_b
Sodium hydroxide	Strong base	NaOH	Very large (∞)
Potassium hydroxide	Strong base	KOH	Very large (∞)
Barium hydroxide	Strong base	$Ba(OH)_2$	Very large (∞)
Ammonia	Weak base	NH_3	6.6×10^{-4}
Aniline (phenylamine)	Weak base	$C_6H_5NH_2$	4.3×10^{-10}

Table 19.5 The dissociation constants of some bases at 25 °C. The value of K_b provides an accurate measure of the extent to which a base dissociates, i.e. the strength of that base.

- Strong bases have relatively large values of K_b.
- Weak bases have small values of K_b.
- As a general rule, if the value of K_b is less than 10^{-2}, the base is classified as a weak base.

The larger the value of K_b, the higher is the concentration of OH^- and the stronger is the base.

Relative strengths of conjugate acid–base pairs

Consider the reaction of the strong acid HCl with water:

$$\underset{\text{strong acid}}{HCl} + H_2O \rightarrow H_3O^+ + \underset{\text{weak base}}{Cl^-}$$

Conjugate acid–base pair

Since HCl is a strong acid, the reaction goes almost completely from left to right, i.e. there is little tendency for the Cl^- ion to accept a proton and push the reaction in the backward direction. Since the Cl^- ion is a poor proton acceptor, we say it is a weak conjugate base.

A **strong acid** has a weak conjugate base.

Now consider the reaction of ethanoic acid (weak acid) and water:

$$\underset{\text{weak acid}}{CH_3COOH} + H_2O \rightleftharpoons \underset{\text{strong base}}{CH_3COO^-} + H_3O^+$$

Conjugate acid–base pair

Since the equilibrium lies on the left-hand side, this implies that the CH_3COO^- ion has a great tendency to accept a proton and push the equilibrium to the left. This means that the CH_3COO^- ion is a good proton acceptor, i.e. it is a strong base.

A **weak acid** has a strong conjugate base.

From studying a large number of acid–base reactions, chemists have deduced the following general statements.

The stronger the acid, the weaker is its conjugate base.
The weaker the acid, the stronger is its conjugate base.

Example 19.4

Question

Define (a) acid, (b) conjugate pair, in terms of the Brønsted–Lowry theory.

Sulfuric acid dissociates in water as follows: $H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$

Why is (i) sulfuric acid considered to be a strong acid, (ii) the conjugate base of sulfuric acid described as a weak base? Show, by means of an equation, that the conjugate base of sulfuric acid can itself act as an acid. [LCH]

Answer

(a) An acid is a proton donor.

(b) A conjugate acid–base pair is any pair consisting of an acid and a base which differ by one proton.

(i) Sulfuric acid is a strong acid because it is a good proton donor, i.e. it is almost fully dissociated into ions in aqueous solution.

(ii) The conjugate base of sulfuric acid, HSO_4^-, is described as a weak base because it is a poor proton acceptor, i.e. it has little tendency to accept a proton to form H_2SO_4. Since H_2SO_4 is a strong acid, the equilibrium $H_2SO_4 + H_2O \rightleftharpoons H_3O^+ + HSO_4^-$ lies very much on the right-hand side.

The following equation shows that the conjugate base of sulfuric acid can itself act as an acid:

$$HSO_4^- + H_2O \rightarrow H_3O^+ + SO_4^{2-}$$

Do not get confused between the words '**concentrated**' and '**strong**'. As already discussed in Chapter 12, a concentrated solution is one that contains a large amount of solute in a given volume of solution. In chemistry, the word 'strong' refers to the extent to which an acid can donate H^+ ions. Unfortunately, in everyday speech we use the word 'strong' to mean concentrated. Instead of asking for a cup of strong coffee, you should really ask for a cup of concentrated coffee! Table 19.6 summarises how the terms *concentrated*, *dilute*, *strong* and *weak* differ in this context.

ACIDS AND BASES	
STRENGTH	**CONCENTRATION**
A **strong acid** is a good proton donor.	A **concentrated solution** of a strong acid contains a large amount of acid dissolved in a small amount of water. A **dilute solution** of a strong acid contains a small amount of acid dissolved in a large amount of water.
A **strong base** is a good proton acceptor.	A **concentrated solution** of a strong base contains a large amount of base dissolved in a small amount of water. A **dilute solution** of a strong base contains a small amount of base dissolved in a large amount of water.
A **weak acid** is a poor proton donor.	A **concentrated solution** of a weak acid contains a large amount of acid dissolved in a small amount of water. A **dilute solution** of a weak acid contains a small amount of acid dissolved in a large amount of water.
A **weak base** is a poor proton acceptor.	A **concentrated solution** of a weak base contains a large amount of base dissolved in a small amount of water. A **dilute solution** of a weak base contains a small amount of base dissolved in a large amount of water.

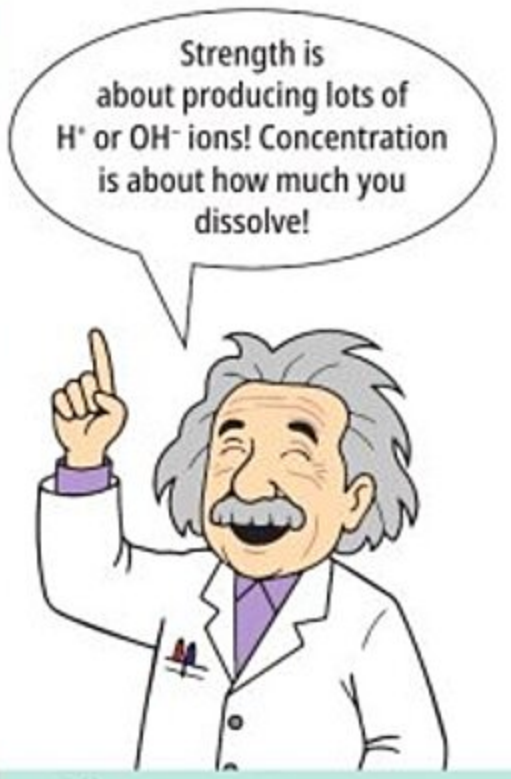


Table 19.6 It is important that you understand the terms *concentrated*, *dilute*, *strong* and *weak* when studying the properties of acids and bases.

pH is a measure of acidity but not of acid strength

- Measuring the pH of a solution does not allow us to distinguish between a strong acid and a weak acid.
- The pH of a solution tells us the concentration of H^+ ions in moles per litre in that solution.
- Imagine adding a few drops of concentrated sulfuric acid (strong acid) into a large volume of water. You could adjust the volume of water so that the pH of the final solution is 5.0, i.e. there are 1×10^{-5} moles of H^+ ions per litre, Figure 19.9.
- Now imagine adding a larger amount of concentrated ethanoic acid (acetic acid), a weak acid, into a smaller volume of water. You could adjust the volume of water so that the pH of the final solution is 5.0.
- In short, making up a dilute solution of a strong acid, or a concentrated solution of a weak acid, can give the same pH value.

While strong acids fully dissociate and weak acids only partly dissociate in water, the final pH of their solutions only depends on the concentration of H^+ ions per litre (and the temperature of course, but let's assume that the temperature is constant). The pH sensor that is inserted into the solution measures the concentration of H^+ ions per litre and it does not matter how they got there! Think carefully about this!

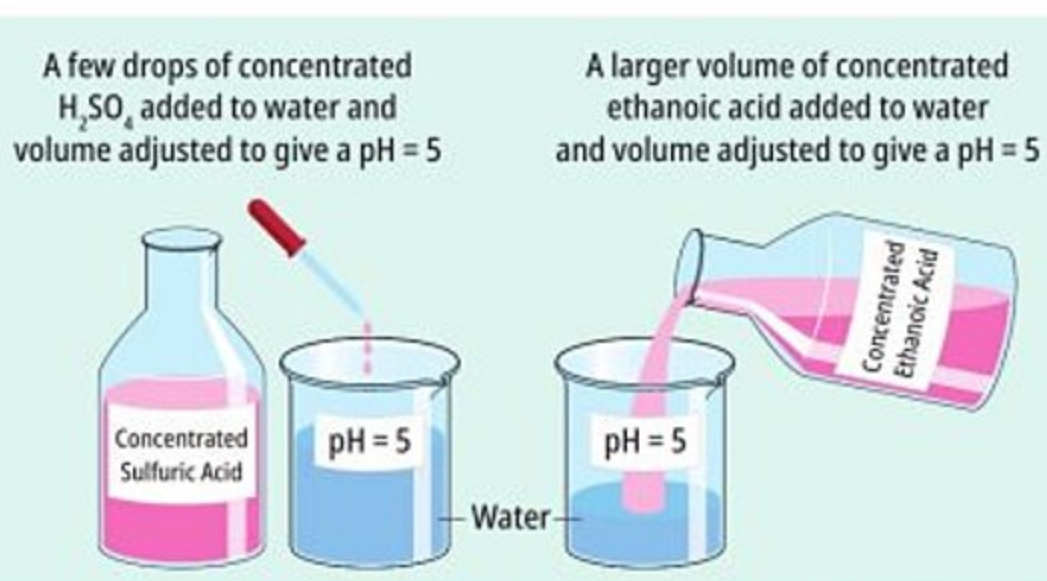

A few drops of concentrated H_2SO_4 added to water and volume adjusted to give a pH = 5
A larger volume of concentrated ethanoic acid added to water and volume adjusted to give a pH = 5
Concentrated Sulfuric Acid
pH = 5
Water
pH = 5
Concentrated Ethanoic Acid

Figure 19.9 Measurement of pH alone does not allow us to distinguish between a weak acid and a strong acid. The dilute solution of sulfuric acid (strong acid) and the concentrated solution of ethanoic acid (weak acid) have the same pH.

Example 19.5

Question

A teacher was left gasping for air on reading a statement written in a student's exam script that said, 'Solutions of strong acids always have a low pH.' Explain why this statement is not correct.

Answer

- pH depends on the concentration of H^+ ions in solution.
- A strong acid is defined as a good proton donor.
- A strong acid is almost fully dissociated into ions in aqueous solution.
- If you take, say, one drop of a strong acid such as HCl or H_2SO_4, and dilute it by adding it to a large volume of water, the resulting concentration of H^+ ions will be very low.
- The pH of this solution could be around 4 or 5 or even higher, depending on how dilute the solution is.
- For example, the pH of a 0.00001 M solution of HCl = 5. In other words, the dilute solution of this strong acid does **not** have a low pH.
- On the other hand, the pH of a 0.1 M solution of the weak acid ethanoic acid (acetic acid) = 2.9. In other words, the more concentrated solution of this weak acid had a lower pH than the more dilute solution of the HCl (strong acid).
- Therefore, it is incorrect to say that solutions of strong acids always have a low pH. This confuses the level of acidity present in solution with the strength of an acid. The pH is determined by the concentration of H^+ ions in solution – not by whether the acid is a strong acid or a weak acid.

It is possible to work out on paper the pH of a solution if we have certain information about that solution. In this course, you are required to be able to calculate the pH of solutions of (a) strong acids and strong bases and (b) weak acids and weak bases. We now consider these two types of calculation.

19.5 Calculating the pH of strong acids and strong bases

Calculating the pH of strong acids and strong bases is very straightforward, since strong acids and strong bases can be assumed to be fully dissociated in water. The following examples will illustrate the method used.

Example 19.6

Question

Calculate the pH of a 0.01 M HCl solution.

Answer

Since the acid is fully dissociated, the 0.01 mole of HCl will give 0.01 mole of H^+ ions in solution.

$$HCl \rightarrow H^+ + Cl^-$$

$$1 \text{ mole} \rightarrow 1 \text{ mole}$$

$$\therefore 0.01 \text{ mole} \rightarrow 0.01 \text{ mole}$$

$$pH = -\log_{10}[H^+] = -\log_{10}(0.01) = 2$$

Answer: pH = 2

Example 19.7

Question

Calculate the pH of a solution containing 5 g of sulfuric acid in 250 cm^3 of solution.

Answer

Step 1

Calculate the concentration of the acid in grams per litre.

5 g H_2SO_4/250 cm^3 = 20 g H_2SO_4/L

Step 2

Convert this mass to number of moles.

$$\text{No. of moles of } H_2SO_4 = \frac{\text{Mass}}{\text{Rel molecular mass}} = \frac{20}{98.086} = 0.204$$

i.e. concentration of H_2SO_4 solution = 0.204 mol/L

$2 \times H = 2 \times 1.008$	=	2.016
$1 \times S = 1 \times 32.07$	=	32.07
$4 \times O = 4 \times 16.00$	=	64.00
$M_r\ H_2SO_4$	=	98.086

Step 3

Calculate the concentration of moles of H^+ ions per litre.

$H_2SO_4 \rightarrow 2H^+ + SO_4^{2-}$

1 mole → 2 moles H^+ ions

∴ 0.204 mole → 0.408 mole H^+ ions

Step 4

Calculate the pH.

$pH = -\log_{10}[H^+] = -\log_{10}(0.408) = 0.3893$

Answer: pH = 0.3893

A similar method is used to find the pH of a solution of a strong base. We know from our study of the ionic product of water at 25 °C that: $[H^+][OH^-] = 10^{-14}$

Taking the negative log of each term: $pH + pOH = 14$

Thus, pOH is defined in a similar fashion to pH: $pOH = -\log_{10}[OH^-]$

Example 19.8

Question

Calculate the pH of a 0.15 M NaOH solution.

Answer

Step 1

Calculate the number of moles of OH^- ions in solution.

$NaOH \rightarrow Na^+ + OH^-$

1 mole → 1 mole

∴ 0.15 mole → 0.15 mole

Step 2

Calculate the pOH.

$pOH = -\log_{10}[OH^-] = -\log_{10}(0.15) = 0.82$

Step 3

Calculate the pH.

pH = 14 – pOH = 14 – 0.82 = 13.18

Answer: pH = 13.18

Note that to calculate the pH of a solution of a base, we first work out the pOH and subtract this value from 14.

$$pH = 14 - pOH$$

Example 19.9

Question

Calculate the pH of a solution containing 9 g of potassium hydroxide, KOH, in 500 cm^3 of solution.

Answer

Step 1

Calculate the concentration of the KOH in grams per litre.

9 g KOH/500 cm^3 = 18 g KOH / litre

Step 2

Convert grams per litre to moles per litre.

$$\text{No. of moles of KOH} = \frac{\text{Mass}}{\text{Rel. molecular mass}} = \frac{18}{56.108} = 0.3208$$

Therefore, concentration of KOH = 0.3208 mol/L

$1 \times K = 1 \times 39.1$	= 39.1
$1 \times O = 1 \times 16.00$	= 16.00
$1 \times H = 1 \times 1.008$	= 1.008
M_r KOH	= 56.108

Step 3

Calculate the number of moles per litre of OH^- ions in solution

$$KOH \rightarrow K^+ + OH^-$$

1 mole → 1 mole

$\therefore$ 0.3208 mole → 0.3208 mole OH^-

Step 4

Calculate the pOH.

$pOH = -\log_{10}[OH^-] = -\log_{10}(0.3208) = 0.4938$

Step 5

Calculate the pH.

pH = 14 – pOH = 14 – 0.4938 = 13.5062

Answer: pH = 13.5062

Example 19.10

Question

Calculate the pH of a 0.01 M solution of calcium hydroxide, $Ca(OH)_2$. Assume that the calcium hydroxide is fully dissociated.

Answer

Step 1

Calculate the number of moles of OH^- ions per litre.

$Ca(OH)_2 \rightarrow Ca^{2+} + 2OH^-$

1 mole → 2 mole

$\therefore$ 0.01 mole → 0.02 mole

Step 2

Calculate the pOH

$pOH = -\log_{10}[OH^-]$

$= -\log_{10}(0.02)$

$= 1.7$

Step 3

Calculate the pH

$pH = 14 - pOH$

$= 14 - 1.7$

$= 12.3$

Answer: pH = 12.3

Note: Since the pH scale is a logarithmic one, a difference in one pH unit corresponds to a ten-fold difference in the concentration, Table 19.7.

(a)

Concentration of HCl solution	pH
1.0 M	0
0.1 M	1
0.01 M	2
0.001 M	3
0.0001 M	4

(b)

Concentration of NaOH solution	pH
1.0 M	14
0.1 M	13
0.01 M	12
0.001 M	11
0.0001 M	10

Table 19.7 The logarithmic nature of the pH scale is illustrated by studying the pH values of **(a)** solutions of HCl of various concentrations and **(b)** solutions of NaOH of various concentrations.

TEST YOURSELF: Attempt Questions 19.4–19.5 and W19.4–W19.5.

19.6 Calculating the pH of weak acids and weak bases

To calculate the pH of a solution of a weak acid or weak base, we must know the extent to which the acid or base dissociates. This depends on the value of the dissociation constant for the acid or base. (K_a or K_b) and also on the concentration of the solution. To explain how the pH is calculated, we will first work out the pH of a solution from first principles, and then use this to deduce a general expression for solving similar problems.

Example 19.11

Question

Calculate the pH of a 0.1 M solution of ethanoic acid given that the value of K_a is 1.8×10^{-5} at 25 °C.

Answer

Let x = number of moles of H^+ ions produced.

	CH_3COOH	$\rightleftharpoons$	CH_3COO^-	+	H^+
Initially	[0.1]		[0]		[0]
At equil.	[0.1 – x]		[x]		[x]

Now write the dissociation constant (K_a) expression for this reaction and substitute the above equilibrium concentrations into the expression.

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]}$$

$$1.8 \times 10^{-5} = \frac{(x)(x)}{(0.1 - x)}$$

To make it easier to solve this equation, we make the assumption that $0.1 - x \approx 0.1$. This is a valid assumption since, for a weak acid, the amount of dissociation is very small.

Thus, the above expression now simplifies to:

$$\frac{(x)(x)}{0.1} = 1.8 \times 10^{-5}$$

$$x^2 = 1.8 \times 10^{-5} \times 0.1$$

$$x = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.3 \times 10^{-3}$$

i.e. $[H^+] = 1.3 \times 10^{-3}$

$pH = -\log_{10}[H^+] = -\log_{10}(1.3 \times 10^{-3}) = 2.9$

Answer: pH = 2.9

In the above problem, we obtain a very simple expression at the end.

$$x = \sqrt{1.8 \times 10^{-5} \times 0.1}$$

We can write a more general expression as:

$[H^+] = \sqrt{K_a \times M_{acid}}$
where M_{acid} is the concentration of the acid in moles per litre.

This is a very useful formula for finding the concentration of hydrogen ions (in moles per litre) in a solution of a weak acid when given the value of K_a and the concentration of the acid in moles per litre. It is important to remember that all concentrations are measured in moles per litre.

Similarly, it can be shown that the concentration of OH^- ions in a solution of a weak base is given by:

$[OH^-] = \sqrt{K_b \times M_{base}}$
where M_{base} is the concentration of the base in moles per litre.

The two formulas above are well worth learning off, as they are not given in the *Formulae and Tables* booklet and they greatly simplify the calculations involved in determining the pH values of weak acids and bases, as shown in the following examples.

Example 19.12

Question

Calculate the pH of a 0.1 M solution of methanoic acid (formic acid) given that K_a for this acid is 2.1×10^{-4}. [LCH]

Answer

Step 1

Calculate the $[H^+]$ by substitution in the formula:

$$[H^+] = \sqrt{K_a \times M_{acid}} = \sqrt{2.1 \times 10^{-4} \times 0.1} = \sqrt{0.000021} = 0.0046$$

Step 2

Calculate the pH.

$$pH = -\log_{10}[H^+] = -\log_{10}(0.0046) = 2.34$$

Answer: pH = 2.34

Example 19.13

Question

Find the pH of an aqueous solution containing 1.48 g of propanoic acid (CH_3CH_2COOH) in 200 cm^3 of solution, given that the dissociation constant K_a for propanoic acid is 1.36×10^{-5}. [LCH]

Answer

Step 1

Calculate the concentration of the propanoic acid in g/L.

1.48 g CH_3CH_2COOH/200 cm^3 = 1.48 × 5 g /L = 7.4 g/L

Step 2

Calculate the number of moles of propanoic acid per litre (molarity of solution).

Rel. molecular mass CH_3CH_2COOH = 74.078

$$\text{No. of moles} = \frac{\text{Mass}}{\text{Relative molecular mass}} = \frac{7.4}{74.078} = 0.0999$$

$\therefore M_{acid} = 0.0999$ mol/L

$3 \times C = 3 \times 12.01$	=	36.03
$6 \times H = 6 \times 1.008$	=	6.048
$2 \times O = 2 \times 16.00$	=	32.00
$M_r\ H_2SO_4$	=	74.078

Step 3

Calculate the concentration of H^+ ions in moles/L.

$$[H+] = \sqrt{K_a \times M_{acid}} = \sqrt{1.36 \times 10^{-5} \times 0.0999} = \sqrt{1.3586 \times 10^{-6}} = 0.0012$$

Step 4

Calculate the pH.

$$pH = -\log_{10}[H^+] = -\log_{10}(0.0012) = 2.92$$

Answer: pH = 2.92

2. Temperature

Temperature is the second factor that affects the pH of a solution, although its effect is more noticeable in weak acids and bases or in pure water.

For weak acids and bases, increasing the temperature generally increases the extent of ionisation.

- This is because the dissociation of most weak acids and weak bases is an endothermic process, meaning it absorbs heat in the forward direction.
- According to Le Chatelier's Principle, if temperature increases, the equilibrium shifts to produce more ions.
- As a result:
  - In a weak acid, increasing temperature produces more H^+ ions in solution, so the pH decreases slightly, Figure 19.11.
  - In a weak base, increasing temperature increases OH^- ions, so the pH increases slightly. An exception to this general statement is ammonia as the reaction between ammonia and water is exothermic. We will look at this exception more closely in the workbook accompanying this textbook.

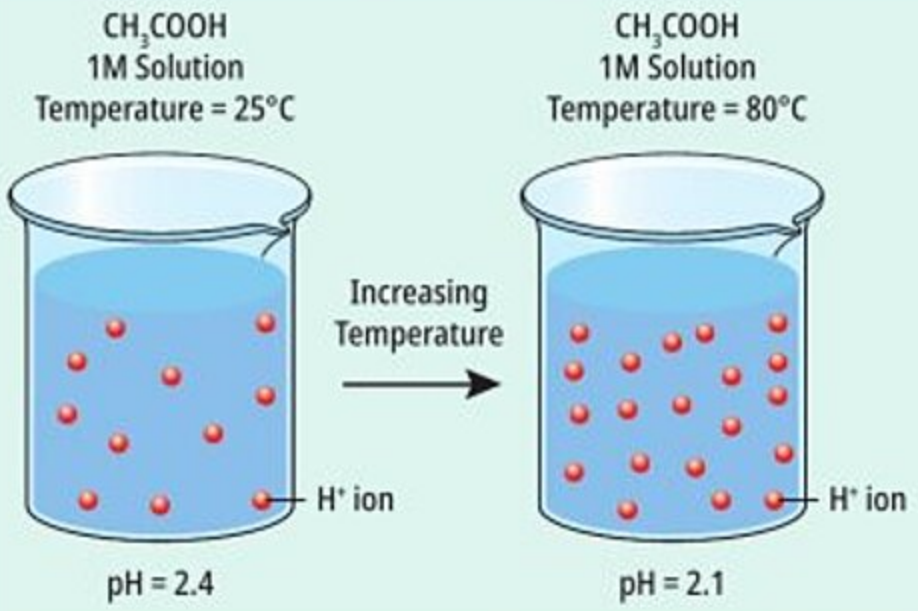


Figure 19.11 Increasing the temperature of the weak acid, ethanoic acid, caused more H^+ ions to be produced and the pH is lowered.

As already discussed, temperature also affects K_w, the ionisation constant of water. At 25 °C, $K_w = 1.0 \times 10^{-14}$, and pure water has a pH of 7.

However, at higher temperatures, K_w increases, meaning water produces more H^+ and OH^- ions.

This means that even pure water at higher temperatures can have a pH below 7, but it is still neutral, because $[H^+] = [OH^-]$.

So while temperature may not always have a dramatic effect on pH, it is important to remember that pH values are temperature-dependent, especially in cases involving weak acids, weak bases, or water itself.

Using a conductivity sensor to distinguish between strong acids and weak acids, and between strong bases and weak bases

You may recall that in Chapter 6 we learned that molten ionic compounds and ionic compounds in solution conduct an electric current. We will now look at this idea of electrical conductivity in a little more detail. The term *electrical conductivity* may be defined as follows.

Electrical conductivity is a measure of how easily an electric current can pass through a substance.

Electrical conductivity in solutions depends on the presence of ions to carry the electric charge. The more ions that are present, the better the solution conducts electricity.

Note: Electrical conductivity taking place in solutions is different to electrical conductivity taking place in metals. When electricity flows through a metal wire, it is electrons that carry the electric charge. However, when an electric current is passed through a solution, it is ions which carry the electric charge. (How these ions carry the charge will be discussed in Chapter 22.)

We can use a scientific instrument called a conductivity sensor to measure electrical conductivity, Figure 19.12.

Figure 19.12 A conductivity sensor measures how well a solution can conduct electricity. Note that the conductivity of the 0.01 M HCl solution is very high.

Summarising the factors that affect the pH of a solution

As we conclude our study of pH, it may be helpful to summarise the two main factors that affect the pH of a solution, as these are specifically mentioned on the syllabus.

1. Concentration of H^+ ions

Since $pH = -\log_{10}[H^+]$, the first and most obvious factor that determines the pH of a solution is the concentration of hydrogen ions measured in moles per litre (mol/L).

- When comparing two solutions of the same acid, the more concentrated the solution, the higher the concentration of H^+ ions – and therefore, the lower the pH.
- Similarly, for two solutions of the same base, the more concentrated the solution, the greater the concentration of OH^- ions – and therefore, the higher the pH.
- However, the actual concentration of H^+ or OH^- ions also depends on whether the acid or base is strong or weak.
  - A strong acid has a large Ka value and dissociates more in water, producing more H^+ ions.
  - A strong base has a large K_b value and produces more OH^- ions in solution.
- Therefore, when comparing two different acids that have equal concentrations:
  - If acid A is strong and acid B is weak, acid A will have a larger K_a and produce more H^+ ions.
  - As a result, the pH of acid A will be lower than the pH of acid B, Figure 19.10.

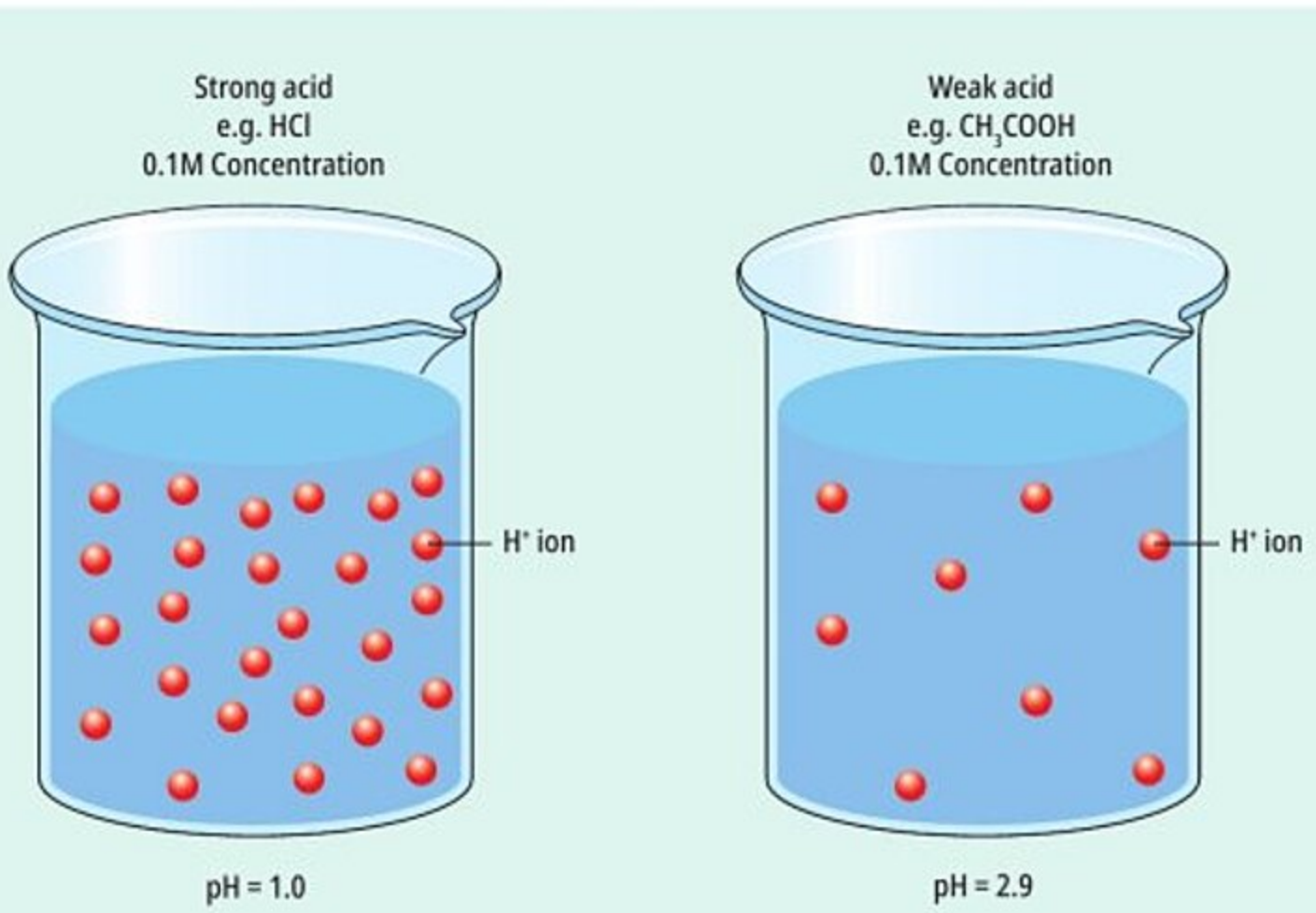


Figure 19.10 Both acids are of equal concentration but the stronger acid produces more H^+ ions in solution and, therefore, has a lower pH than the weak acid.

- Similarly, comparing two different bases of equal concentration:
  - If base A is strong and base B is weak, base A will have a larger K_b and produce more OH^- ions than base B.
  - Therefore, the pH of base A will be higher than the pH of base B.

Since strong acids and strong bases dissociate in solution to give more ions than weak acids and weak bases, we can use a conductivity sensor to distinguish between strong acids and weak acids and also distinguish between strong bases and weak bases. To ensure a fair test, we compare the conductivity of a 0.01 M solution of hydrochloric acid (strong acid) and a 0.01 M solution of ethanoic acid (weak acid), Figure 19.13. (Dilute solutions are used as the conductivity of strong acids is very high.)

A conductivity sensor is placed in each solution in turn and the results are displayed on a computer screen. Note that the conductivity of the strong acid (12,014.0) is much higher than that of the weak acid (213.0). (The units of conductivity are micro siemens per cm, but you do not need to worry about these units.)

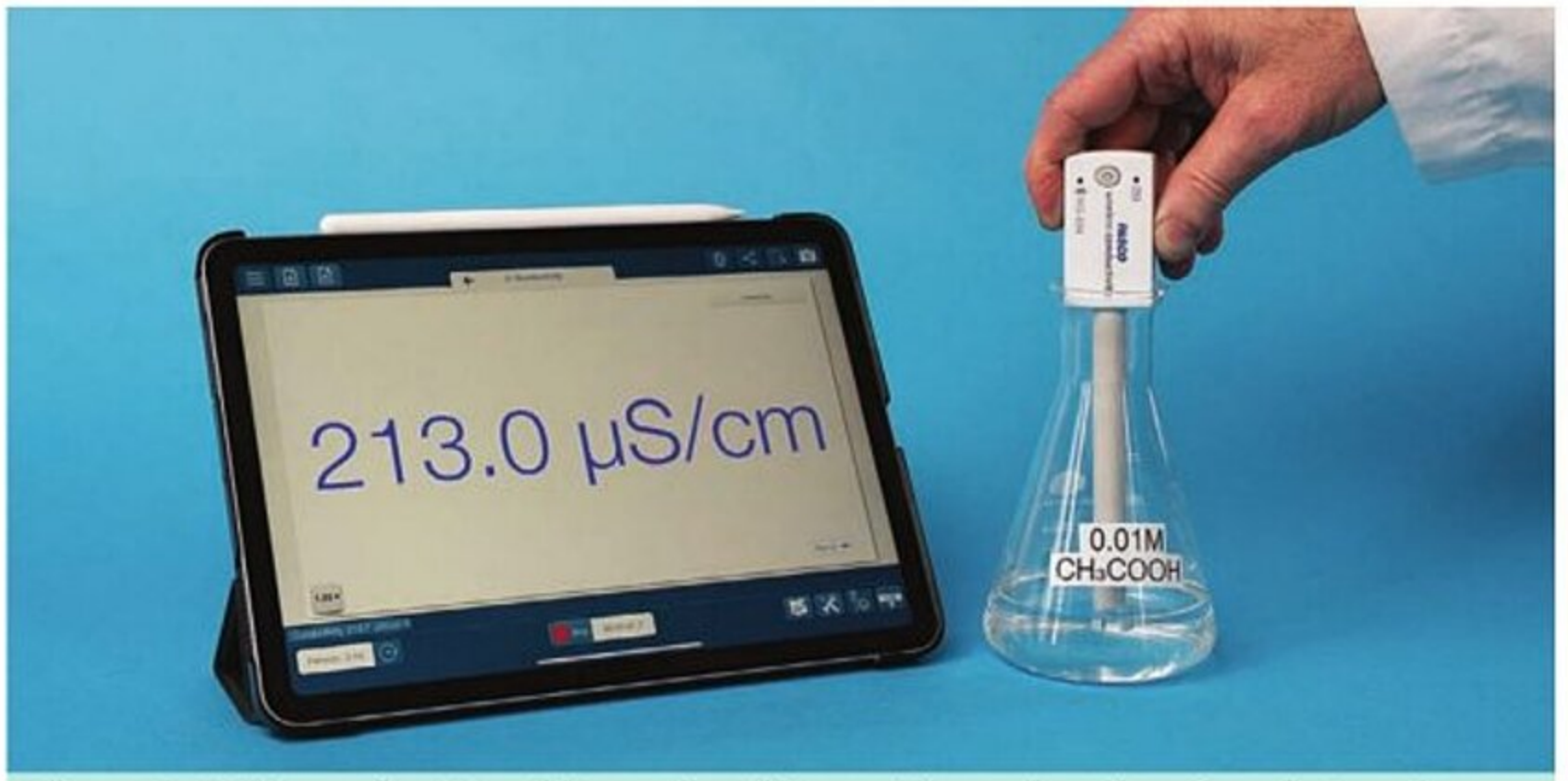


Figure 19.13 The conductivity of the weak acid is much lower than that of a solution of a strong acid of the same concentration. Conductivity depends on the number of ions in solution. Since the strong acid produces more ions in solution than the weak acid, the conductivity of the strong acid is much higher than the weak acid.

Limitations of the pH scale

We have seen that the concept of pH is extremely useful in chemistry and is one of the foundations of the study of chemistry. However, it is helpful to be aware of some limitations of the pH scale.

1. Limited to 0–14. The pH scale is limited to the 0–14 range even though, in theory, pH values outside this range are possible. We will give examples of this in the next point.

2. Limited to dilute solutions (< 1 M). The pH scale does not work with very concentrated solutions. For example, the pH of 1 M HCl is 0 and that of 1 M NaOH is 14. It is found that once the concentration goes above 1 M, complete dissociation does not always occur, i.e. you cannot predict the actual number of H^+ or OH^- ions in solution. Therefore, calculations of pH for solutions of concentration greater than 1 M are not accurate. For example, if you calculate the pH of 10 M HCl solution using the formula $pH = -\log_{10}[H^+]$, you obtain a pH value of –1. Similarly, if you calculate the pH value of 10 M NaOH solution, you obtain a pH value of 15. However, these calculations are based on the assumption that full dissociation occurs and this is not the case with very concentrated solutions. In short, pH is limited to dilute solutions of 1 M or less.

3. Limited to aqueous solutions. The pH scale is limited to solutions in which substances are dissolved in water (aqueous solutions). However, chemical reactions can occur in other types of solvent, such as ethanol and liquid ammonia. These need not concern us in this course.

TEST YOURSELF:
Attempt Questions 19.6–19.11 and W19.6–W19.15.

19.7 Acid–base indicators

In Chapter 12, we saw that acid–base indicators were used to find the end point when carrying out a titration. We now consider the theory used to explain how these indicators work, and we discuss how to choose an indicator for a particular titration.

An **acid–base** indicator is a substance that changes colour according to the pH of the solution in which it is placed.

The main points about acid–base indicators may be summarised as follows:

- Many natural dyes act as indicators, e.g. the dye in red cabbage, elderberry juice and blackberry juice. Examples of indicators that you meet in the school laboratory are litmus, methyl orange and phenolphthalein, Figure 19.14. Litmus is obtained from plants called lichens that grow on cliffs and trees. Acid–base indicators are often simply referred to as 'indicators'.

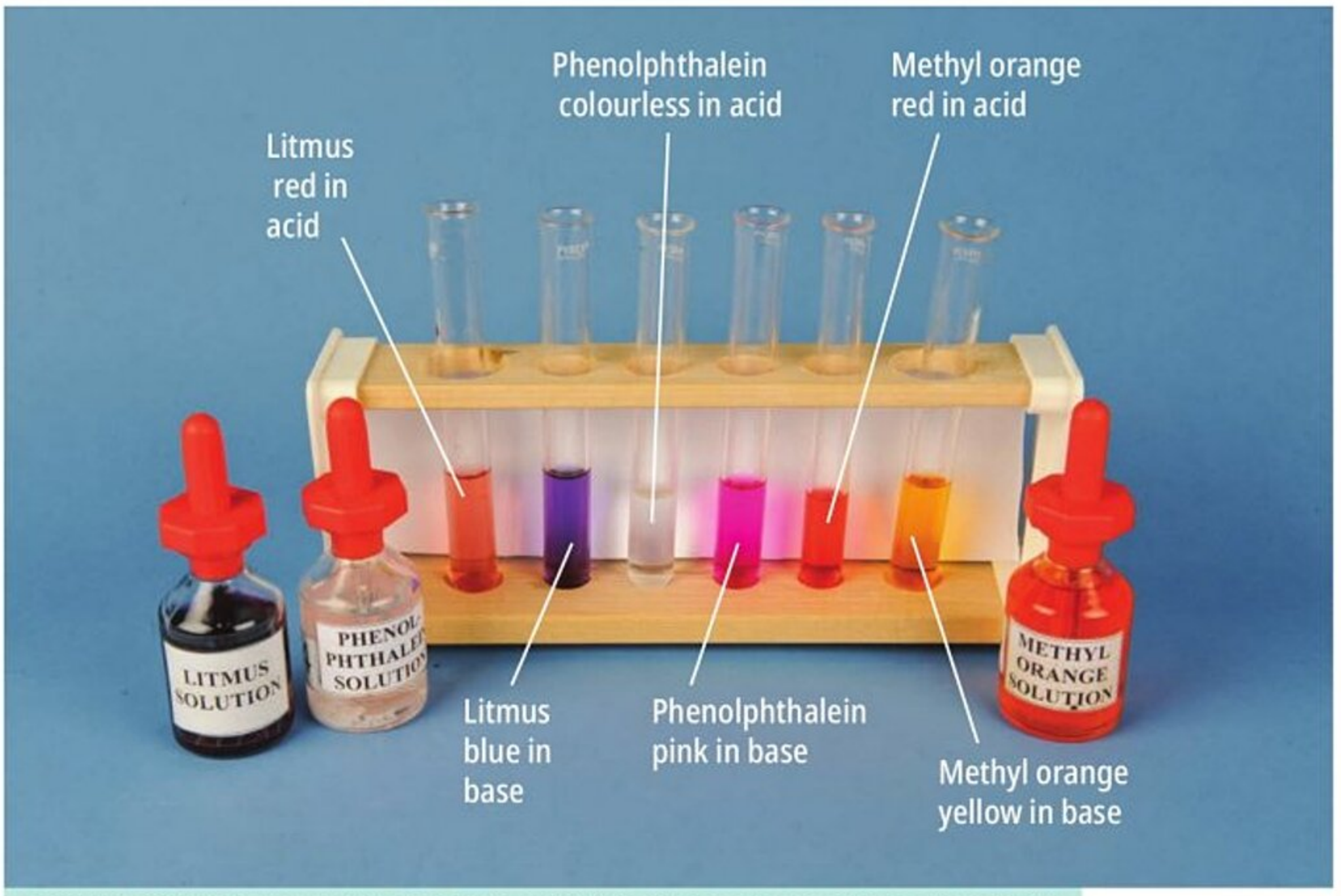


Figure 19.14 Methyl orange, litmus and phenolphthalein are common acid–base indicators.

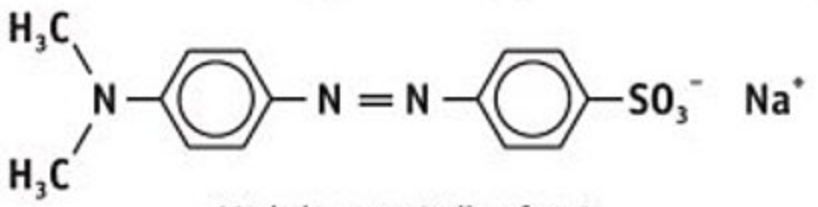
- Most indicators are weak acids in which the colour of the undissociated molecule is different from that of the dissociated molecule. (In reality, the dissociated molecule is the negative ion of the indicator.) Suppose we represent the indicator litmus as HIn. Litmus has a red colour in an acidic solution and is blue in an alkaline solution.

$$\underset{\text{red}}{\underset{\textbf{(acid)}}{HIn}} \rightleftharpoons \underset{\text{blue}}{\underset{\textbf{(base)}}{H^+ + In^-}}$$

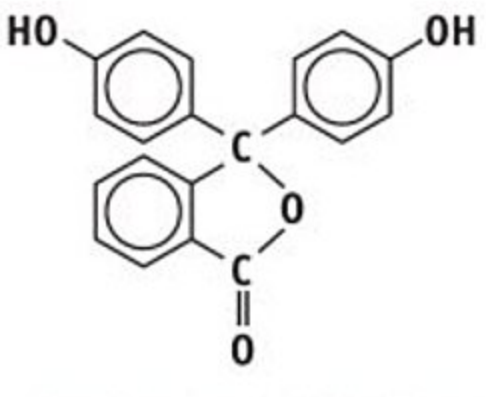
- HIn represents the acid form of the indicator and In^- represents the conjugate base of the indicator. If H^+ ions from an acid are added to blue litmus, the blue litmus turns red. This is because, in accordance with Le Chatelier's Principle, the above equilibrium shifts from right to left in order to absorb the added H^+ ions. Therefore, the red colour of the HIn predominates. In other words, the blue litmus turns red.
- If a base containing OH^- ions is added to red litmus, the OH^- ions react with the H^+ ions in the above equilibrium reaction to remove them to form water. In accordance with Le Chatelier's Principle, more H^+ ions must be formed and, therefore, the equilibrium is shifted to the right. Thus, the blue colour of the In^- ions predominates. In other words, the red litmus turns blue.
- A small number of indicators are weak bases that dissociate slightly as follows:

$$XOH \rightleftharpoons X^+ + OH^-$$

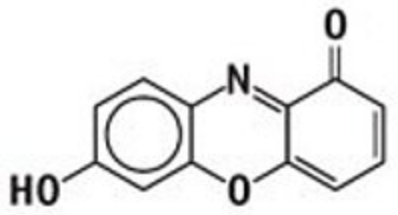
- The undissociated XOH part has a different colour to the dissociated X^+ part. Addition of acid removes some of the OH^- ions from the right-hand side as water, and thus the equilibrium shifts to the right. Therefore, the colour of X^+ predominates in acidic solution.
- Addition of base increases the concentration of OH^- ions on the right-hand side and this shifts the equilibrium to the left-hand side. Hence the colour of XOH predominates in basic solution.
- When an indicator is used in a titration, there is usually very little of it used, e.g. only two or three drops of an indicator are added to 25 cm^3 of the solution in the conical flask. Therefore, the indicator makes a negligible contribution to the H^+ (or OH^-) ion concentration.
- The molecules of indicators tend to be rather complicated, with lots of benzene rings! Some examples of these molecules are shown in Figure 19.15. (Litmus is actually a mixture of a number of dyes but the structure common to many of the dyes is shown in Figure 19.15.) You do not have to remember the structures of any of these molecules. They are simply included to brighten up your lives!



Methyl orange (yellow form)



Phenolphthalein (colourless form)



Litmus (common structure)

Figure 19.15 The molecules of the indicators litmus, methyl orange and phenolphthalein are fairly complicated. There is no need to remember them!

Range of an indicator

Because our eyes have limited sensitivity to colour changes, it is found that indicators need a change of about two pH units in order for us to see a distinct change from one colour to another. The pH interval over which there is a clear change of colour for a particular indicator is called the **range** of the indicator.

The **range of an indicator** is the pH interval over which there is a clear change of colour for that indicator.

Each indicator has its own range, and examples of the ranges of common indicators are given in Table 19.8.

Name of indicator	Approx. range	Acid colour (lower pH)	Base colour (higher pH)
Methyl orange	3–5	red	yellow
Litmus	5–8	red	blue
Phenolphthalein	8–10	colourless	pink

Table 19.8 The ranges of some common indicators

From Table 19.8 we can conclude the following:

- Methyl orange has a distinct red colour below a pH of 3 and a distinct yellow colour above a pH of 5. Between a pH of 3 and 5, the indicator is neither distinctly red nor yellow but an intermediate colour.
- Litmus has a definite red colour below a pH of 5 and a definite blue colour above a pH of 8.
- Phenolphthalein is colourless below a pH of 8 and has a definite pink colour above a pH of 10.

It is recommended that you learn Table 19.8 by heart, as this information will be very useful to you.

- The pH ranges of different indicators vary, i.e. indicators change colour over widely differing pH values. This is because each indicator has its own dissociation constant value.
- You may recall that universal indicator is a mixture of indicators that gives a gradual change in colour over the entire range of the pH scale, Figure 19.16. A few drops of universal indicator are added to a solution whose pH is to be measured and the colour observed is compared with a colour chart supplied with the universal indicator. This gives an approximate value of the pH of the solution.

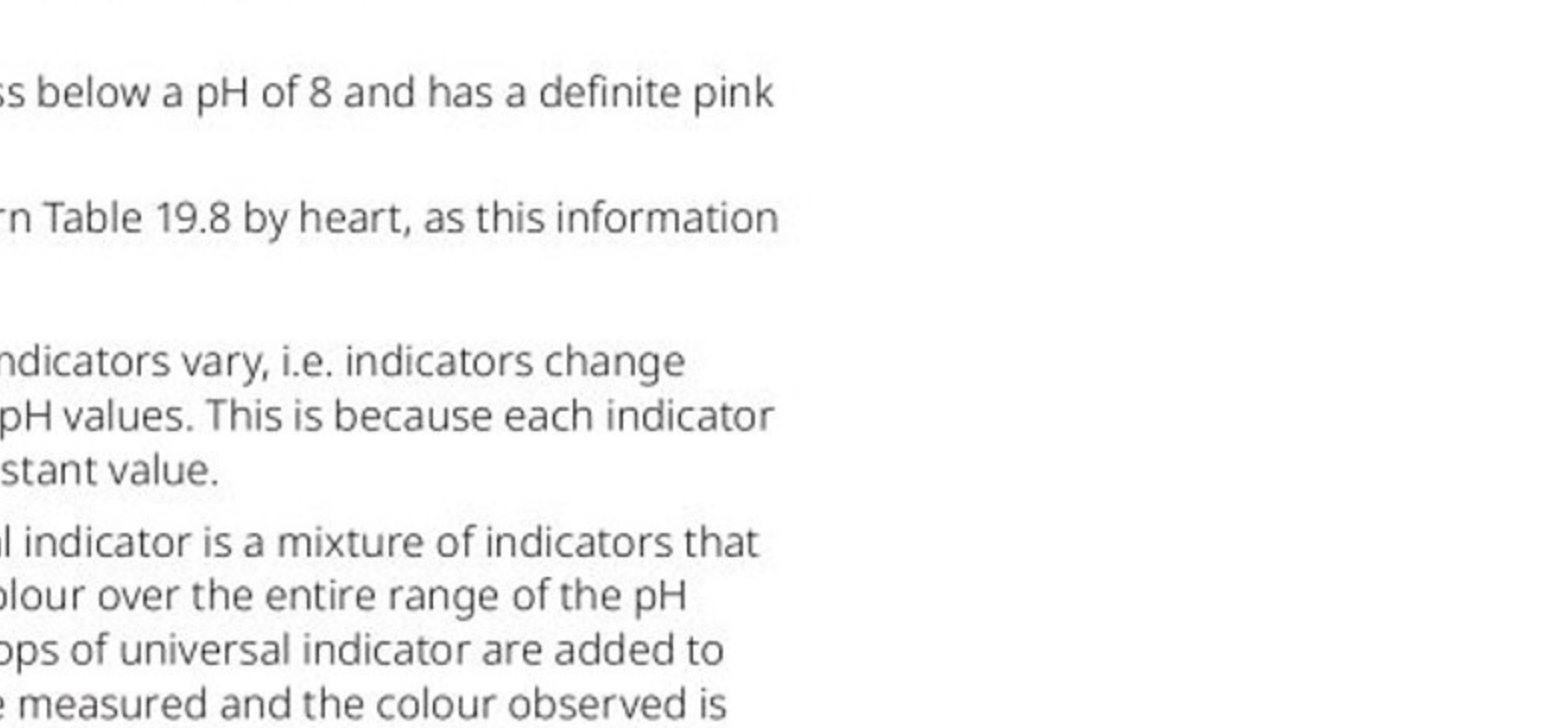


Figure 19.16 Universal indicator has been added to solutions whose pH ranges (left to right) from 1 to 14. The colour observed is then compared with a pH colour chart supplied with the indicator.

Measuring pH accurately using a pH sensor

The most accurate way of measuring pH is to use an instrument called a pH sensor, Figure 19.17. A pH sensor is also called a pH probe or pH electrode. It is a more accurate way of measuring pH than using pH indicators for the following reasons:

1. Precise numerical value. A pH sensor always gives a precise numerical value for pH, e.g. pH = 4.72. It does this by measuring the voltage set up by hydrogen ion concentration and converts this to an exact digital pH measurement. Since a pH sensor is measuring electrical signals, it works perfectly and accurately regardless of the colour of the solution.

2. Removes subjectivity. A pH sensor does not rely on subjective colour interpretation, which can vary between people when estimating shades of colour using pH indicators. The colour of pH indicators can also be affected by the colour of the solution itself or by lighting in the room. pH indicators may suggest that the pH of a solution is approximately 3–4 but a more accurate value is not possible as you are only judging shades of colour.

As a result, pH sensors are ideal for scientific experiments where high precision is needed. For example, in a titration you may wish to know when the pH of the solution is exactly equal to 7. Only a pH sensor can give this level of precision.

Figure 19.17 A pH sensor is the most accurate way to measure pH values. This wireless PASCO pH sensor connects to a laptop or mobile phone using Bluetooth.

Calibrating pH sensors: accuracy and precision

Before using pH sensors in an experiment, we must calibrate the sensor. Calibration is the process of ensuring that the pH sensor is giving accurate pH readings. To do this, we set the pH sensor to correct pH values using solutions of known pH values.

Why is calibration necessary for pH sensors?

- The pH sensor is a very sensitive, accurate and delicate instrument and must always be handled with great care.
- A pH sensor responds to the concentration of H^+ ions in solution.
- Over time, the sensitivity of the pH probe can drift due to wear and tear (ageing) of the sensor, contamination of the sensor with previous solutions, or drying out of the glass bulb of the sensor.

- One of the most common causes of drift is the drying out of the glass bulb due to incorrect storage. When not in use, a pH sensor must always be stored in the storage solution supplied with the pH sensor. Otherwise, the pH sensor can dry out in the air and will not function properly. The pH sensor then has to be left stored for several hours in the storage solution to get it functioning again.

When calibrating a pH sensor, we usually use two different buffer solutions.
See Figure 19.18.

Figure 19.18 This pH sensor is being calibrated using buffer solutions of pH 3 and pH 10.

A **buffer solution** is one that resists change in pH on the addition of small amounts of acid or base.

In other words, the pH of a buffer solution stays constant, even if we add small amounts of acid or base. Buffer solutions are ideal for calibrating pH sensors since buffer solutions have a known, fixed pH. To calibrate the pH sensor, we must have a standard reference, i.e. something we know is correct. Buffer solutions are our standard references in calibration.

You may recall in Chapter 13 that we explained that **accuracy** means how close a measurement is to the correct value. The correct value is often referred to as the 'true' or 'actual' value. Since calibration adjusts the sensor's response to match known standards of pH buffer solutions, this makes the reading **accurate**.

After the electrode has been calibrated, repeated readings could be taken to test for **precision**. You may recall in Chapter 13 that precision means how close a set of repeated measurements are to each other. For example, if you place the pH electrode in deionised water and obtain readings of 7.00, 7.01 and 7.00, you know that these readings are both accurate and precise. However, if you were to obtain readings of 7.40, 6.35 and 6.91, you would know that these readings are neither accurate nor precise.

Carrying out a pH titration

It is quite easy to follow the changes in pH as a titration is carried out. Such an experiment is called a **pH titration** and the experimental set up is shown in Figure 19.19.

The main points about this experiment may be summarised as follows:

- The base is placed in the burette and the acid is placed in a beaker. This is done to allow us to start with a low pH value and work upwards.
- You will recall that we used a conical flask when previously carrying out titrations. We do not use a conical flask when performing pH titrations as the narrow mouth of the conical flask would make it difficult to insert the pH sensor properly – it would get in the way of the burette. The beaker is better for pH titrations as it allows the pH sensor to be kept upright or resting against the side of the beaker when the tip of the pH sensor is immersed in the solution. But how do we stir the solution in the beaker during the titration? Stay tuned!
- The solution in the beaker is kept stirred by placing a small magnetic stirring bar in the beaker. Since we are not using a conical flask, shaking the beaker could cause spillages and could damage the pH sensor. Instead, the solution in the beaker is stirred with the aid of the magnetic stirring bar. The beaker is placed on a laboratory magnetic stirrer and this keeps the stirring bar rotating.
- A pH sensor is placed in the acid solution. As already explained, the pH sensor is a device that measures the hydrogen ion concentration in a solution and displays the corresponding pH value.
- The pH sensor measures the pH as the base is added from the burette to the acid in the beaker.
- The pH sensor is connected to a computer or mobile phone using Bluetooth wireless technology.
- A graph of *pH versus time* is plotted for the solution in the beaker with the aid of the datalogging software. A graph showing change of pH related to volume of base added is obtained. This graph is called a **pH titration curve**.
- Note that no indicator is used in this titration. It is not necessary as we are measuring the pH directly using the pH sensor and, therefore, can see the end point from the pH titration curve.

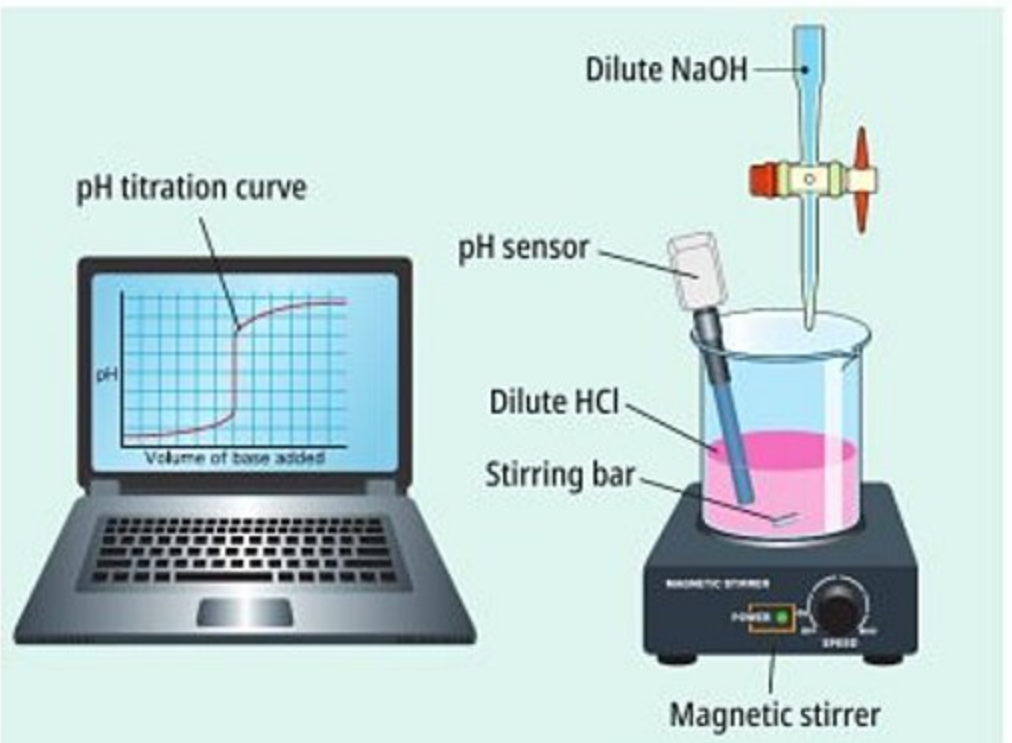


Figure 19.19 In carrying out a pH titration, the acid is usually placed in a beaker and the base is placed in a burette. The pH is measured using a pH sensor. The pH sensor is connected to the laptop using Bluetooth technology. The datalogging software in the laptop or mobile phone detects the signal from the pH sensor and displays the information on the screen.

A photograph of this experiment being carried out is shown in Figure 19.20.

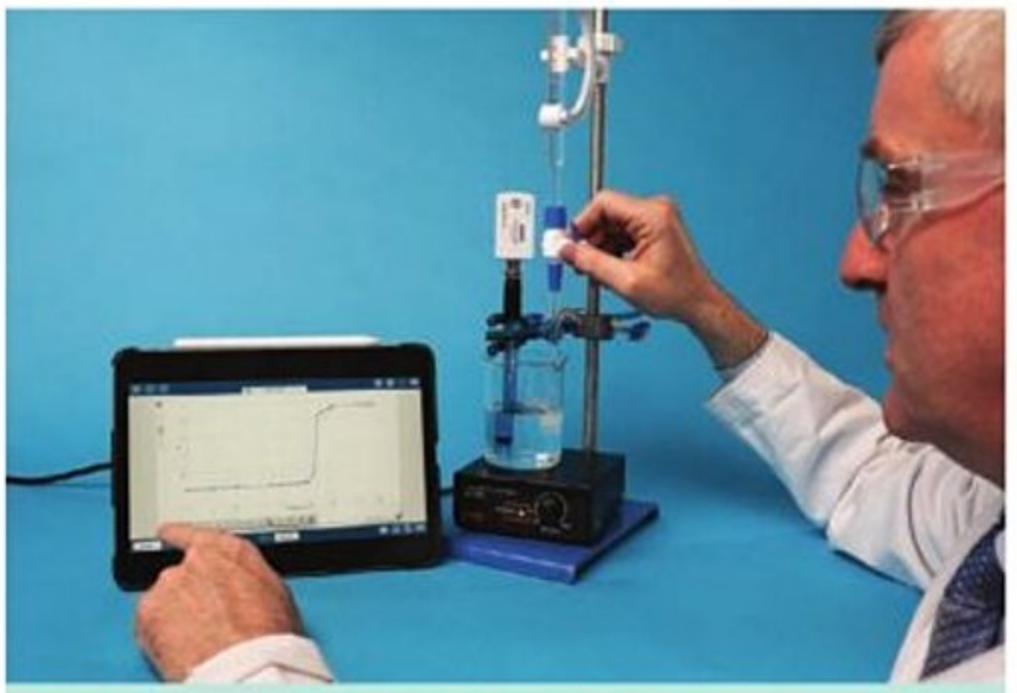


Figure 19.20 A pH titration enables us to follow the changes in pH as the titration proceeds.

We will now consider each of the four possible types of acid–base titration.

1. Titrating a strong acid against a strong base

Consider the pH changes that take place when we titrate a strong acid against a strong base, Figure 19.21.

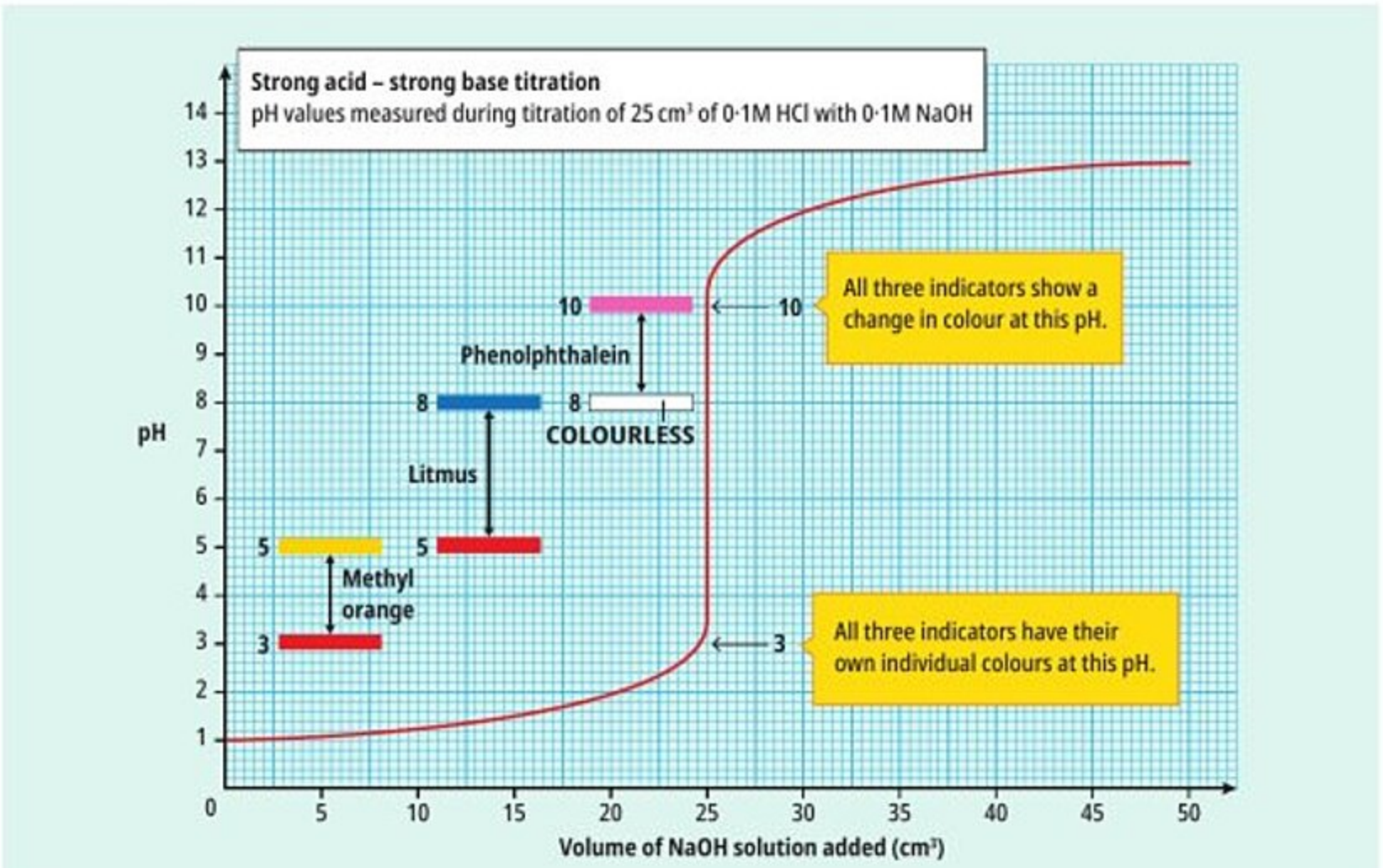

Strong acid – strong base titration
pH values measured during titration of 25 cm³ of 0·1M HCl with 0·1M NaOH
pH
Volume of NaOH solution added (cm³)
Phenolphthalein
Litmus
Methyl orange
10
8
5
3
COLOURLESS
All three indicators show a change in colour at this pH.
All three indicators have their own individual colours at this pH.

Figure 19.21 This graph shows the pH changes observed as a strong acid is titrated against a strong base. The acid is placed in the beaker so that the graph starts with a low pH. Litmus, methyl orange and phenolphthalein are all suitable indicators for this titration.

What indicator would be suitable for this titration?

- Any indicator that has one colour at a pH of around 3 and another colour at a pH of around 10 will identify the end point accurately.
- In other words, we need an indicator that has one colour at the **bottom** of the steep vertical part of the curve and another colour at the **top** of the steep vertical part of the curve.
- Chemists often express this idea by saying that the end point must be 'sharp', i.e. a very small addition of acid or base (one drop) must cause a complete colour change in the indicator.
- Referring to Table 19.8, we see that all three indicators satisfy this criterion. Therefore, all three indicators would be suitable for carrying out a titration of a strong acid against a strong base.
- Litmus is not as reliable as the other two indicators, and hence is not usually used in accurate work.

When carrying out titrations, we used the idea of end point.

The **end point** is the moment during a titration when the indicator changes colour.

There is another point that chemists refer to when discussing pH titration curves.

The **equivalence point** in an acid–base titration is the point at which the acid and the base have reacted in exact proportions according to the balanced equation.

In other words, the equivalence point is the point in the reaction at which both acid and base have reacted in exactly equal amounts according to the mole ratio in the balanced equation. Neither the acid nor the base is present in excess. For example, if you study Figure 19.20, the equivalence point for the strong acid-strong base reaction is at pH = 7. This occurs when 25 cm^3 of 0.1 M NaOH have been added to 25 cm^3 of 0.1 M HCl. At this stage, the same number of moles of acid has reacted with an equal number of moles of base to form a neutral solution of sodium chloride.

In short, the end point is an observable concept and the equivalence point is a chemical concept.

A pH titration could also be carried out by adding the acid to the base. In this case, the pH titration curve starts at a high pH as shown in Figure 19.22.

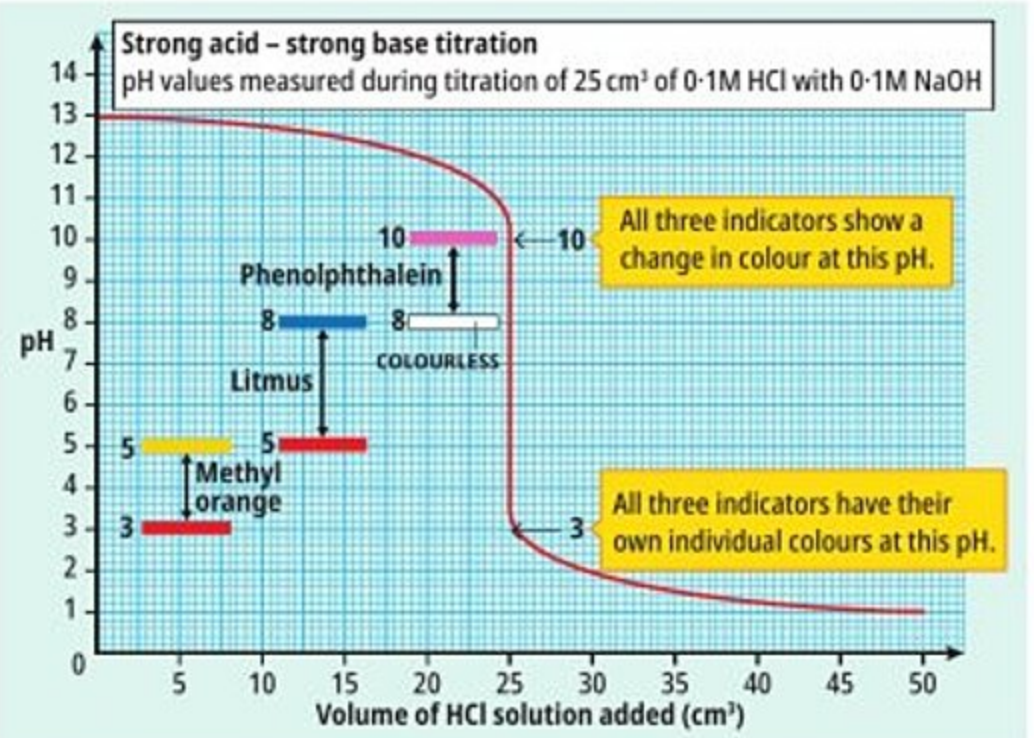

Strong acid – strong base titration
pH values measured during titration of 25 cm³ of 0·1M HCl with 0·1M NaOH
pH
Volume of HCl solution added (cm³)
Phenolphthalein
Litmus
Methyl orange
COLOURLESS
All three indicators show a change in colour at this pH.
All three indicators have their own individual colours at this pH.

Figure 19.22 This graph shows the pH changes observed as a strong acid is titrated against a strong base. The base is placed in the beaker so that the graph starts with a high pH.

2. Titrating a strong acid against a weak base

Consider how the pH changes when a strong acid is titrated against a weak base, Figure 19.23.

What indicator would be suitable for this titration?

- In this titration, 0.1 M NH_3 solution is slowly added to 25 cm^3 of 0.1 M HCl.
- Note that the curve is almost vertical from pH values of 3–7 approximately.
- Therefore, any indicator which has one colour at pH = 3 and another colour at pH = 7 will identify the end point accurately.
- Referring to Table 19.8, we see that the only one of the three indicators that would be suitable is **methyl orange** as it is the only indicator whose range lies within the steep vertical part of the graph.
- Litmus would not be suitable as it would not have completely changed colour until a pH of 8 had been reached.
- Phenolphthalein would not be suitable as its range is completely outside the 3–7 range. In fact, phenolphthalein would not begin to change colour until a pH of 8 was reached.

This pH titration could also be carried out by adding the acid to the base. In this case, the pH titration curve starts at a higher pH as shown in Figure 19.24.

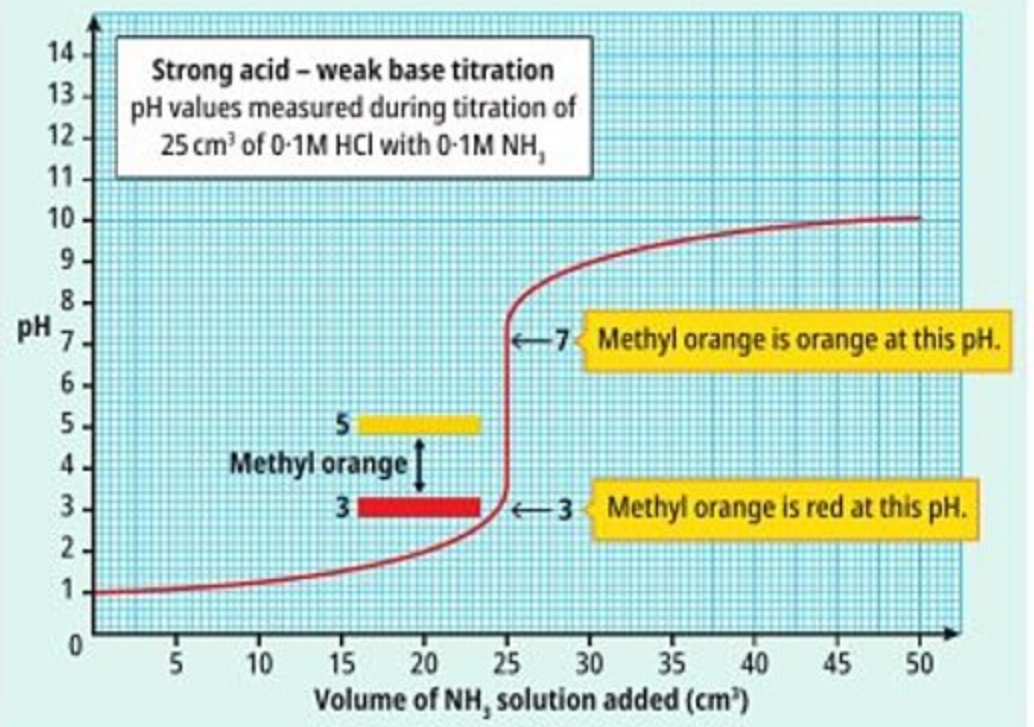

Strong acid – weak base titration
pH values measured during titration of 25 cm³ of 0·1M HCl with 0·1M NH₃
pH
Volume of NH₃ solution added (cm³)
Methyl orange
Methyl orange is orange at this pH.
Methyl orange is red at this pH.

Figure 19.23 This graph shows the pH changes observed as a strong acid is titrated against a weak base. The acid is placed in the beaker so that the graph starts with a low pH. Methyl orange is a suitable indicator for this titration.

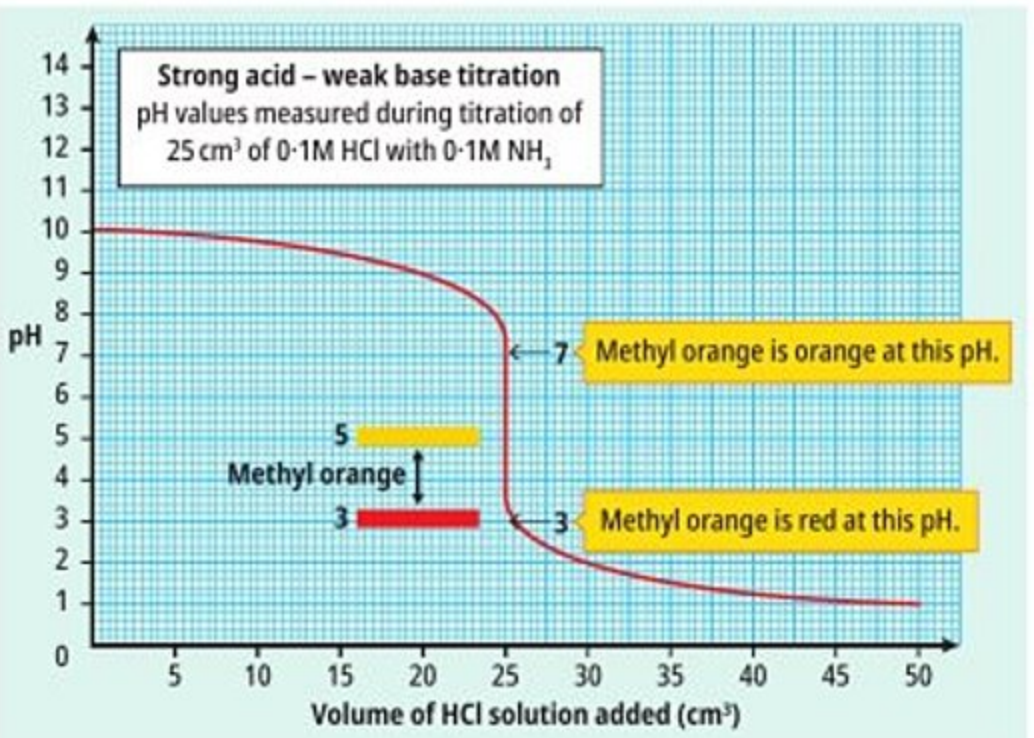

Strong acid – weak base titration
pH values measured during titration of 25 cm³ of 0·1M HCl with 0·1M NH₃
pH
Volume of HCl solution added (cm³)
Methyl orange
Methyl orange is orange at this pH.
Methyl orange is red at this pH.

Figure 19.24 This graph shows the pH changes observed as a strong acid is titrated against a weak base. The base is placed in the beaker so that the graph starts with a higher pH than in the previous diagram

3. Titrating a weak acid against a strong base

We now study how the pH changes when titrating a weak acid against a strong base, Figure 19.25.

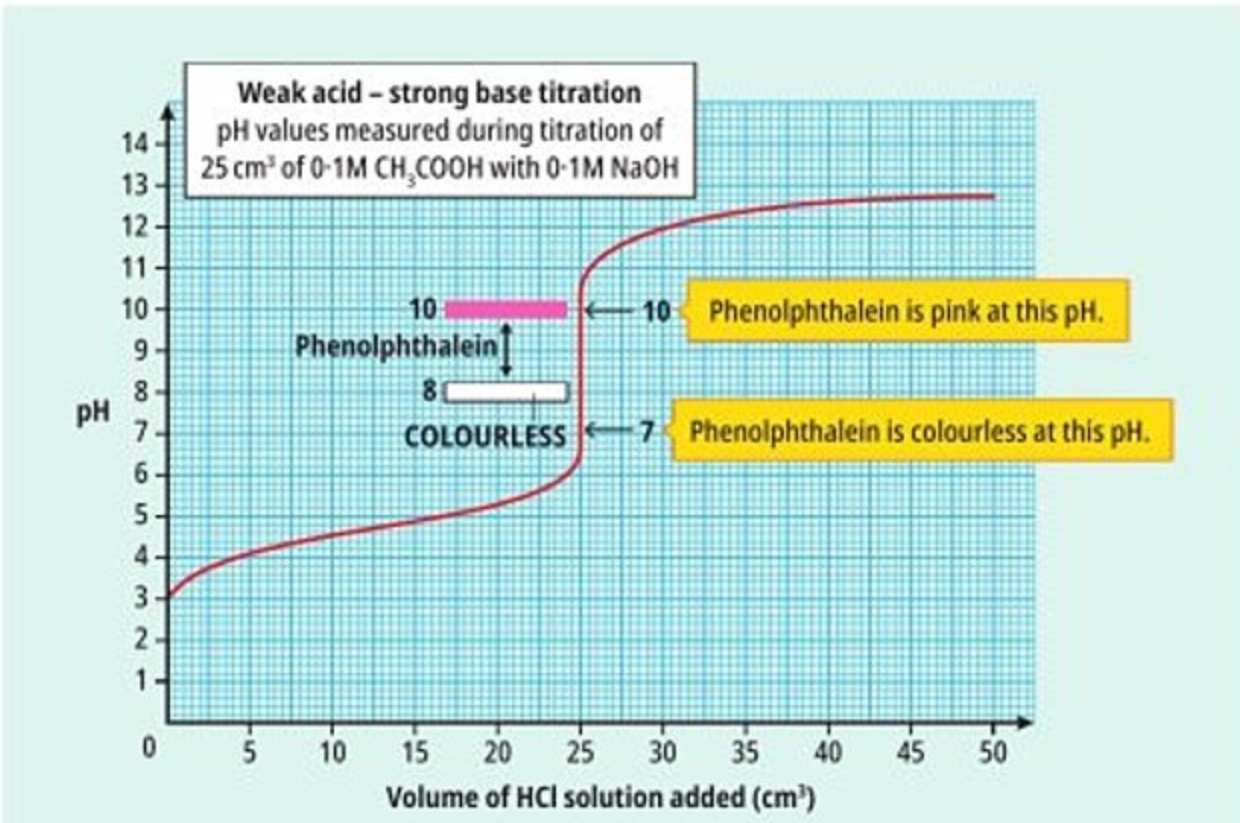


Figure 19.25 This graph shows the pH changes observed as a weak acid is titrated against a strong base. The acid is placed in the beaker so the curve starts at a low pH. Phenolphthalein is a suitable indicator for this titration.

What indicator would be suitable for this titration?

- In this titration, 0.1 M NaOH is slowly added to 25 cm^3 of 0.1 M CH_3COOH.
- Note that the curve is almost vertical from pH values of 7–10 approximately.
- Therefore, we need an indicator which has one colour at pH = 7 and another colour at pH = 10 to identify the end point accurately.
- From Table 19.8, we see that **phenolphthalein** is a suitable indicator for this titration as it is colourless at a pH of 7 and pink at a pH of 10, i.e. its range lies within the steep vertical part of the graph.
- Neither of the other two indicators would be suitable as they are outside the 7–10 range.

This pH titration could also be carried out by adding the acid to the base. In this case, the pH titration curve starts at a higher pH, as shown in Figure 19.26.

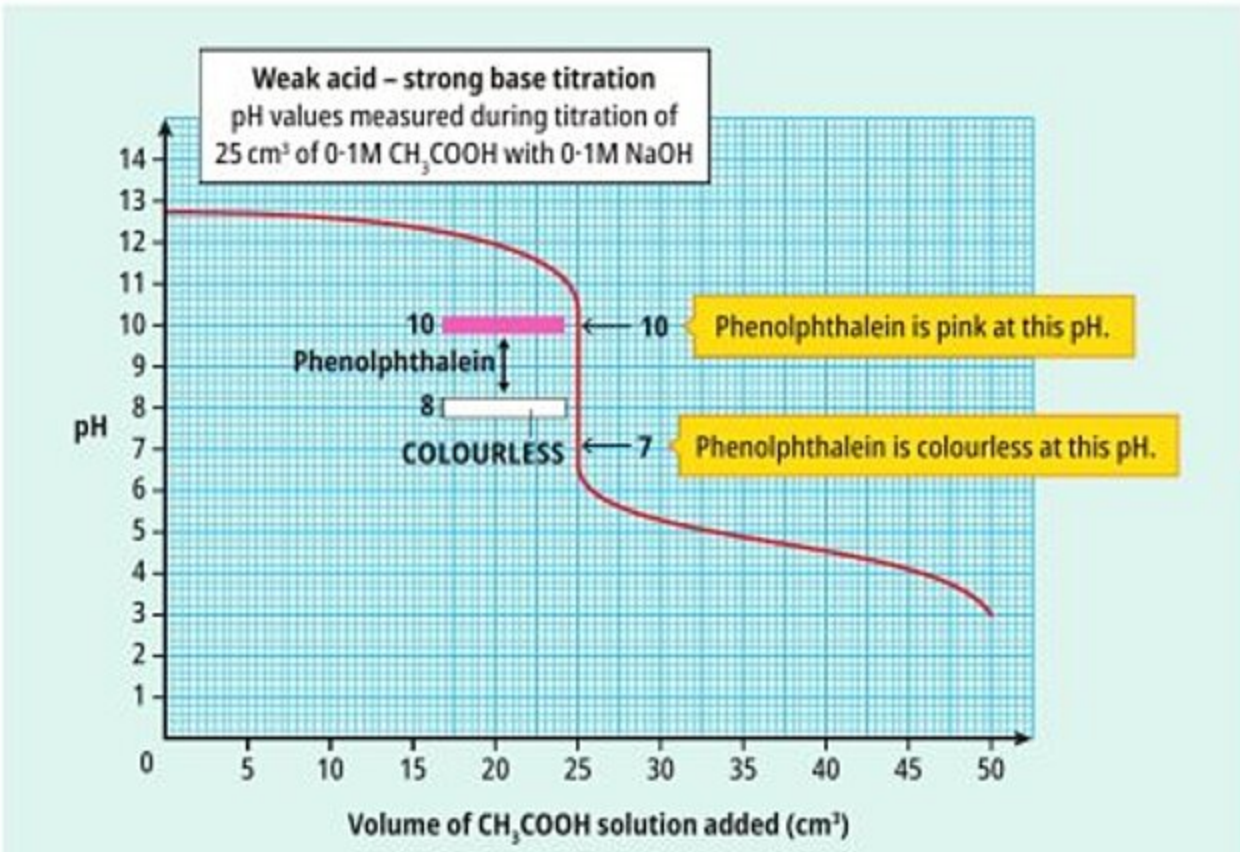


Figure 19.26 This graph shows the pH changes observed as a weak acid is titrated against a strong base. The base is placed in the beaker so that the graph starts with a higher pH than in the previous diagram.

4. Titrating a weak acid against a weak base

Consider how the pH changes when titrating a weak acid against a weak base, Figure 19.27.

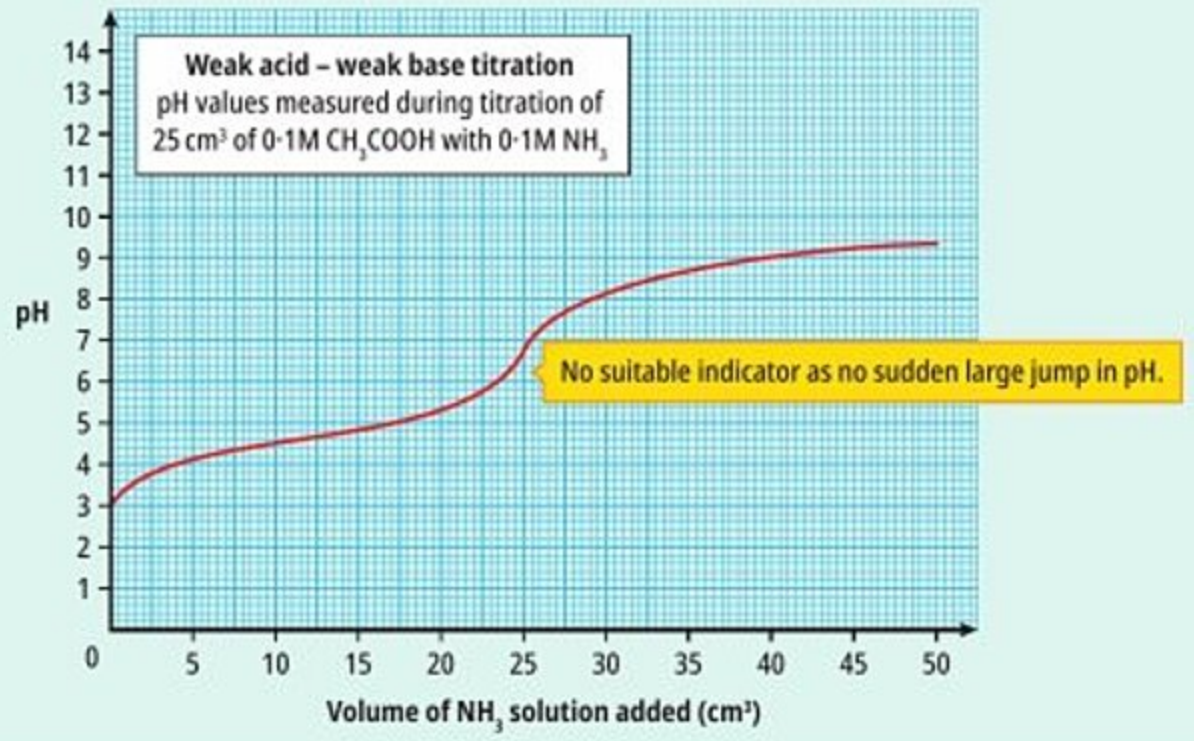

Weak acid – weak base titration
pH values measured during titration of
25 cm³ of 0·1M CH₃COOH with 0·1M NH₃
pH
No suitable indicator as no sudden large jump in pH.
Volume of NH₃ solution added (cm³)

Figure 19.27 This graph shows the pH changes observed as a weak acid is titrated against a weak base. The acid is placed in the beaker so that the graph starts with a low pH. There is no suitable indicator for this titration as there is no sudden increase in the pH at any stage of the titration.

What indicator would be suitable for this titration?

- In this titration, 0.1 M NH_3 is slowly added to 25 cm^3 of 0.1 M CH_3COOH.
- Note that the pH rises so gradually that there is no sudden jump in the pH value at any stage of the titration.
- The graph looks more like a gentle slope rather than having a sharp jump in pH.
- Therefore, it is not possible to detect the end point using an indicator as there would be no large sudden jump in pH to cause a sudden colour change.
- This type of titration could not be used to determine the concentration of a solution of a weak acid or a weak base.
- Instead, the weak acid is titrated against a strong base and the weak base is titrated against a strong acid.

NOTE

When carrying out the above pH titrations, we kept the concentrations of all acids and bases constant at 0.1 M. This was done in order to ensure a fair test. In other words, it allows us to make a fair comparison between the titration curves.

This pH titration could also be carried out by adding the acid to the base. In this case, the pH titration curve starts at a higher pH as shown in Figure 19.28.

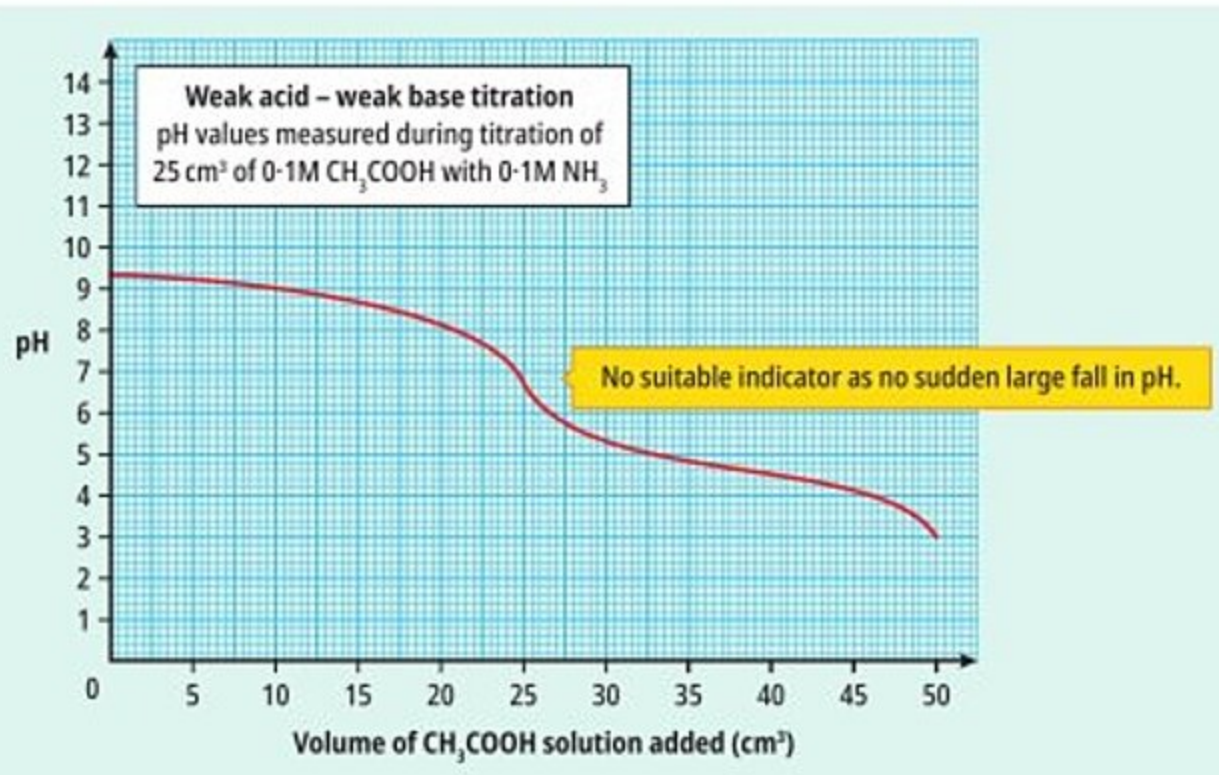
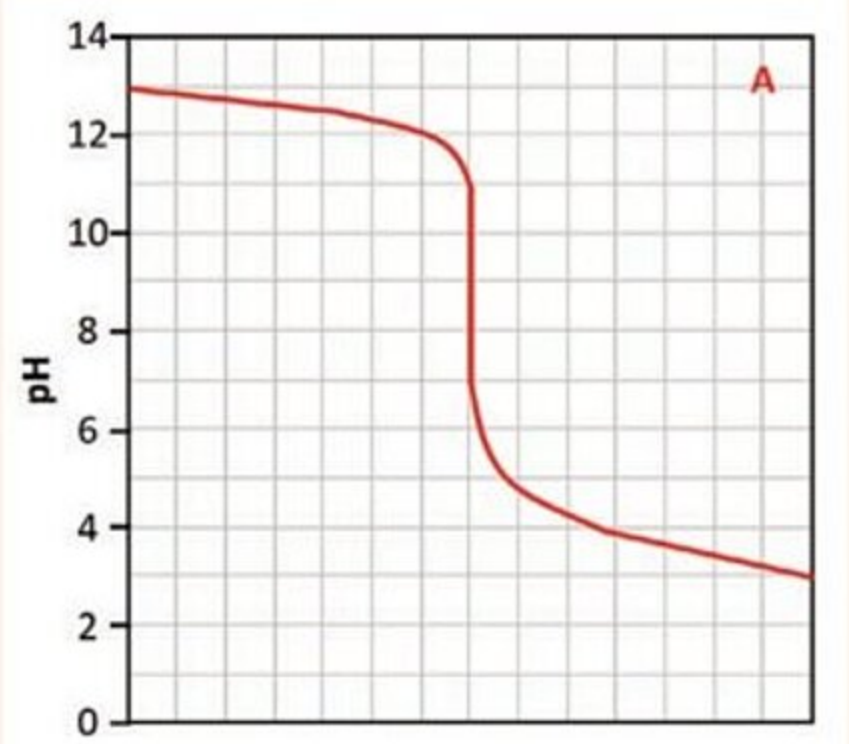

Weak acid – weak base titration
pH values measured during titration of
25 cm³ of 0·1M CH₃COOH with 0·1M NH₃
pH
No suitable indicator as no sudden large fall in pH.
Volume of CH₃COOH solution added (cm³)

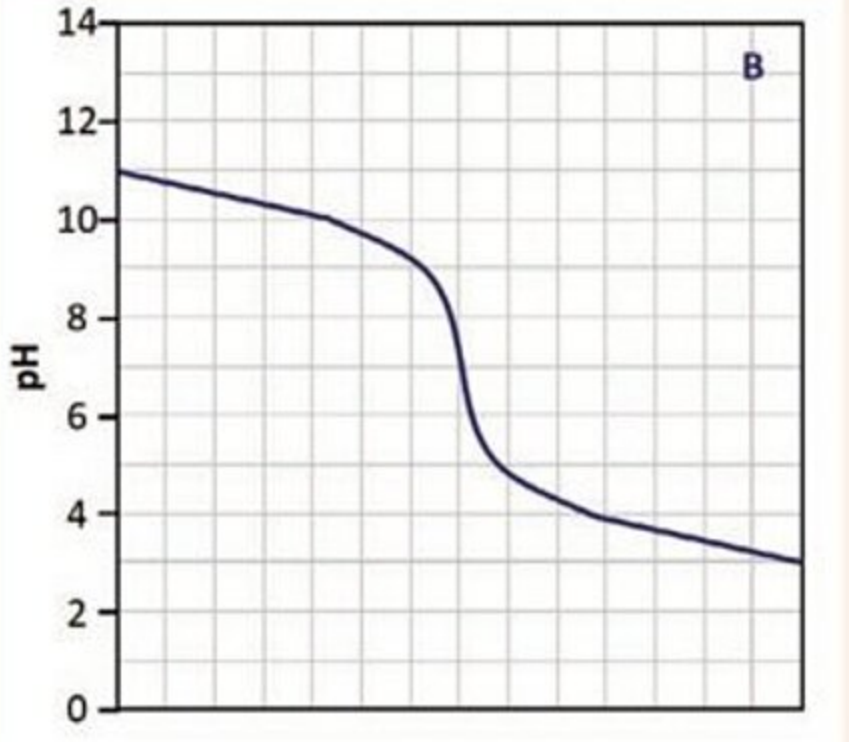
Figure 19.28 This graph shows the pH changes observed as a weak acid is titrated against a weak base. The base is placed in the beaker so that the graph starts with a higher pH than in the previous diagram.

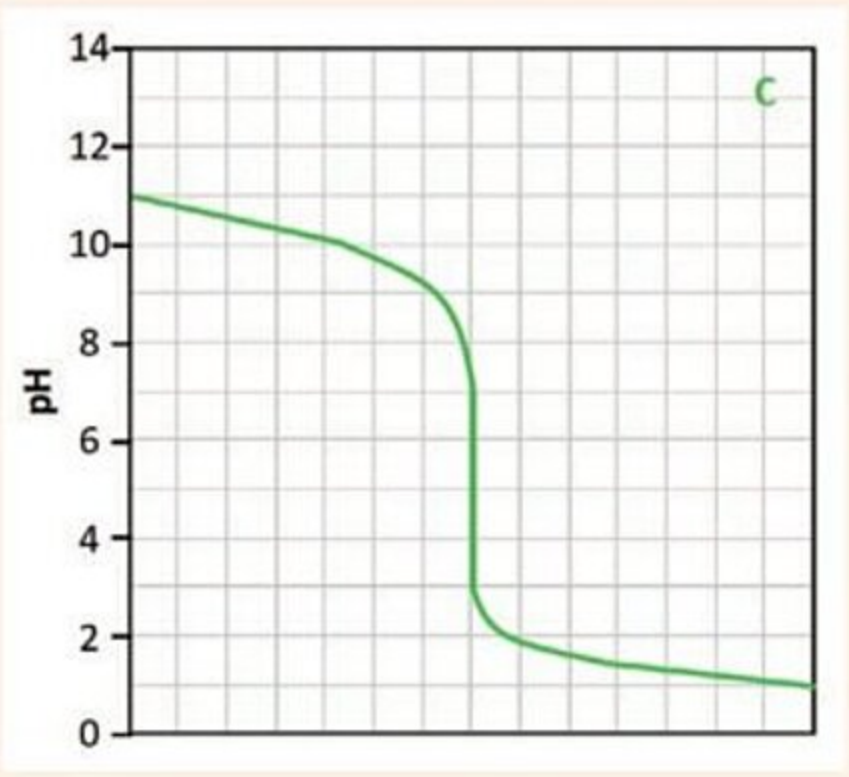
SEC exam question 19.14

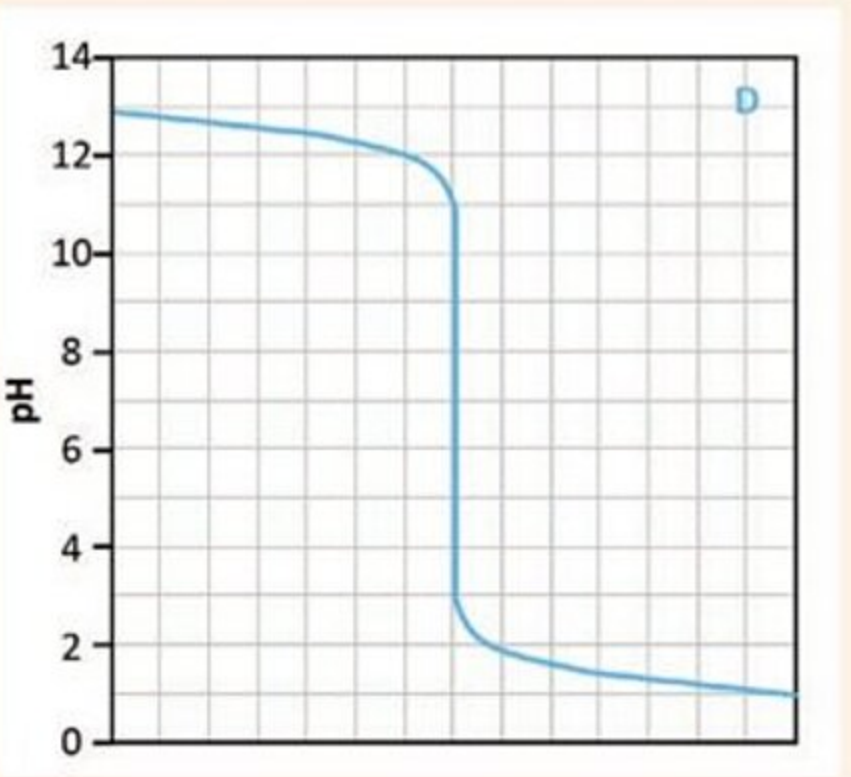
Question

A student carried out a number of acid–base titrations. She used a pH meter to measure how the pH of the solutions changed during each titration. She generated the pH curves shown.









(i) Fill in the table to match the pH curves to the different types of reaction.

Type of reaction	pH curve (A, B, C or D)
strong acid–strong base	D
strong acid–weak base	C
weak acid–strong base	A
weak acid–weak base	B

EXAM TIP!

When asked to identify pH titration curves, it is helpful to write on the curve the lower and upper limits of the vertical part of the curve. For example, curve D has a vertical part of the curve from pH 3 to pH 10. Therefore, this must be the titration curve for a strong acid–strong base titration.

(ii) Explain why it is difficult to carry out an accurate weak acid–weak base titration.

It is difficult to carry out an accurate weak acid–weak base titration because:

- The pH rises so gradually that there is no sudden jump in the pH value at any stage of the titration.
- The graph looks more like a gentle slope rather than having a sharp jump in pH.
- Therefore, it is not possible to detect the end point using an indicator.
- There would be no large sudden jump in pH to cause a sudden colour change in the indicator.

(iii) Explain why the student used a pH meter rather than universal indicator to measure the pH.

The sensor in a pH meter is a more accurate way of measuring pH than using universal indicator for the following reasons:

1. **Precise numerical value.** A pH sensor always gives a precise numerical value for pH, e.g. pH = 4.72. Since a pH sensor is measuring electrical signals, it works perfectly and accurately regardless of the colour of the solution.
2. **Removes subjectivity.** A pH sensor does not rely on subjective colour interpretation, which can vary between people when estimating shades of colour using pH indicators. The colour of universal indicator can also be affected by the colour of the solution itself or by lighting in the room. Universal indicator may suggest that the pH of a solution is approximately 3–4, but a more accurate value is not possible as you are only judging shades of colour.

(iv) Name one variable which the student should have kept constant to make sure that she could make a fair comparison between the titrations.

The concentration of the acid and the concentration of the base should be kept constant to ensure a fair comparison between the titration curves.

TEST YOURSELF: Attempt Questions 19.12–19.18 and W19.16–W19.32.

Summary What I should know

- $K_w = [H^+][OH^-]$. K_w is called the ionic product of water.
- $pH = -\log_{10}[H^+]$ where the square brackets indicate concentration in moles per litre.
- The pH of an acidic solution is less than 7. The pH of an alkaline solution is greater than 7. The pH of a neutral solution is equal to 7 at 25 °C.
- The stronger the acid, the weaker is its conjugate base. The weaker the acid, the stronger is its conjugate base.
- $[H^+] = \sqrt{K_a \times [acid]}$ and $[OH^-] = \sqrt{K_a \times [base]}$ are useful expressions for calculations involving weak acids and weak bases.
- Acid–base indicators are substances that change colour according to the pH of the solution in which they are placed.
- When titrating a strong acid against a strong base, methyl orange, phenolphthalein and litmus are suitable indicators.
- When titrating a strong acid against a weak base, methyl orange is a suitable indicator.
- When titrating a weak acid against a strong base, phenolphthalein is a suitable indicator.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the self-ionisation of water and the ionic product of water.	⬡	⬡	⬡
Define pH and explain the concepts of acid dissociation constant and base dissociation constant.	⬡	⬡	⬡
Calculate the pH of strong acids and strong bases and also of weak acids and weak bases.	⬡	⬡	⬡
Investigate pH titration curves using primary data from acid–base reactions.	⬡	⬡	⬡
Justify the use of certain indicators for particular categories of acid–base reactions.	⬡	⬡	⬡

Chapter review questions

19.1 **(a)** Why does pure water conduct a tiny electric current?

(b) Write down the symbol used to denote the ionic product of water.

(c) Write down the concentration in moles per litre of H^+ ions in pure water at 25 °C.

(d) A solution contains 10^{-9} moles of H^+ ions per litre. Is it acidic or basic?

(e) A solution has a high concentration of H^+ ions. Will it have a high or low pH value? Explain your answer

(f) Write down the pH of a solution which has 10^{-11} moles of H^+ ions per litre.

(g) What is meant by the self-ionisation of water?

(h) Write down the value of the ionic product of water at 25 °C.

(i) How does the value of K_w change with increasing temperature?

(j) Write down the concentration in moles per litre of OH^- ions in pure water at 25 °C.

(k) A solution contains 10^{-3} mole of H^+ ions per litre. Is it acidic or basic?

(l) As the concentration of H^+ ions increases, what happens to the pH value?

(m) As the concentration of H^+ ions decreases, what happens to the pH value?

(n) Write down the pH of a solution which has a concentration of 10^{-5} moles of H^+ ions per litre.

(o) Show by means of an equilibrium equation the self-ionisation of water that occurs even in 'deionised' water.

[LCH]

19.2 Calculate the pH of the following solutions whose hydrogen ion concentrations are:

(a) 10^{-7} mol/L, **(b)** 4.0×10^{-3} mol/L, **(c)** 2.62×10^{-8} mol/L, **(d)** 5.2×10^{-3} mol/L, **(e)** 8.7×10^{-11} mol/L.

19.3 Calculate the hydrogen ion concentration (in moles per litre) of the solutions whose pH values are as follows: **(a)** 5.65, **(b)** 11.15, **(c)** 1.09, **(d)** 7, **(e)** 9.65.

19.4 Calculate the pH of the following solutions: **(a)** 0.1 M HCl, **(b)** 0.01 M H_2SO_4, **(c)** 12.6 g HNO_3 in 500 cm^3 solution, **(d)** 5.48 g HCl in 500 cm^3 solution, **(e)** 5.8 g H_2SO_4 in 250 cm^3 solution.

19.5 Calculate the pH of the following solutions: **(a)** 0.95 M NaOH, **(b)** 5 M NaOH, **(c)** 1 g NaOH in 500 cm^3 solution, **(d)** 0.024 grams KOH per litre, **(e)** 0.37 g $Ca(OH)_2$ per 500 cm^3 solution.

19.6 **(a)** Define the pH of a solution. Explain what is meant by the statement that the dissociation constant of ethanoic acid in aqueous solution is 1.8×10^{-5}.

(b) Find the approximate pH of a solution of 0.3 g ethanoic acid, CH_3COOH, in 50 cm^3 water given that the dissociation constant for ethanoic acid is 1.8×10^{-5}.

19.7 The dissociation constant (K_a) of a monobasic (monoprotic) acid at room temperature is 5.5×10^{-5}. Find the pH of a solution of this acid containing 5.0×10^{-2} mole in 100 cm^3 of the solution.

19.8 **(a)** The dissociation constant of methanoic acid is 1.6×10^{-4} and the dissociation constant of ethanoic acid is 1.8×10^{-5}. Which is the stronger acid?

(b) Calculate the $[H^+]$ in a 0.1 M solution of ethanoic acid given that $K_a = 1.8 \times 10^{-5}$.

19.9 **(a)** The pH of a 1.0 M solution of ethanoic acid is 2.37. Calculate the hydrogen ion concentration and show that the approximate value of the dissociation constant is 1.8×10^{-5}.

(b) What is the approximate value of the pH of a 0.05 M solution of ethanoic acid?

19.10 **(a)** If methanoic acid is 1.3% dissociated in a 1.0 M aqueous solution, show clearly that the approximate value of the acid dissociation constant is 1.7×10^{-4}.

(b) Calculate the pH of the 1.0 M solution of methanoic acid. [LCH]

19.11 The compound $C_2H_5NH_2$ acts as a base by accepting a proton. Calculate the pH of a solution containing 1.5 g of this compound in 250 cm^3 water. K_b for this base is 4.4×10^{-4}.

Chapter review questions

19.12 An indicator called bromothymol blue, represented as HIn, has a yellow colour in the associated form and a blue colour in the dissociated form.

$HIn \rightleftharpoons In^- + H^+$

Use Le Chatelier's Principle to predict the colour change that occurs when **(a)** acid and **(b)** base is added to the indicator.

19.13 **(a)** Explain the terms *strong* and *weak* as applied to acids and bases. The dissociation of an indicator (HIn) which is a weak acid may be represented by:

$HIn \rightleftharpoons H^+ + In^-$

How is the degree of dissociation affected **(i)** by the addition of a strong acid, **(ii)** by the addition of a strong base? Explain your reasoning.

(b) The following table shows the results of titrating 25.0 cm^3 volumes of 0.1 M ethanoic acid solution with a 0.1 M solution of sodium hydroxide using two different indicators.

Indicator	pH range	Volume of sodium hydroxide solution
Methyl Red	4.2–6.3	22.0 cm^3
Phenolphthalein	8.3–10.0	25.0 cm^3

(i) Which is the correct volume of sodium hydroxide solution?

(ii) Explain why the colour change coincided with the end point of the titration for one indicator, but not for the other indicator.

[LCH]

19.14 No indicator will detect the end point when titrating 0.1 M CH_3COOH against 0.1 M NH_3. Explain this observation.

19.15 **(a)** The hydrogen ion concentration in pure water at 25 °C is 1.0×10^{-7} mol/L but at 57 °C it is about 3.0×10^{-7} mol/L. Does this mean that water is acidic at 57 °C? Explain your reasoning.

(b) Methyl red is an indicator used in titrations of strong acids against weak bases. It changes from red to yellow in the pH range 4.2 to 6.3. If it can be regarded as a weak base represented as XOH, explain how it acts as an indicator.

[LCH]

19.16 Explain the principle involved in the use of indicators in acid–base titrations. Suggest suitable indicators for the following titrations: (a) strong acid–strong base, (b) strong acid–weak base, (c) weak acid–strong base.

19.17 Methanoic acid (formic acid) is a weak acid that reacts with sodium hydroxide according to the following equation:

$HCOOH + NaOH \rightarrow HCOONa + H_2O$

(a) What volume of 0.1 M methanoic acid would be needed to neutralise completely 25 cm^3 of 0.108 M sodium hydroxide solution?

(b) Name a suitable indicator for this titration.

(c) Assuming that the indicator you choose is a weak acid, explain briefly how it works.

19.18 A certain indicator is a weak acid ($K_a = 2 \times 10^{-5}$ at 25 °C). Its dissociation in water may be represented as follows:

$HIn_{(aq)} \rightleftharpoons H^+_{(aq)} + In^-_{(aq)}$

(i) Explain the underlined terms.

(ii) What is the approximate pH of a 0.01 M solution of the indicator at 25 °C?

(iii) The indicator changes colour in the pH range 3.7 – 5.7. State the types of acid–base titration for which it would be suitable and explain why it can be used in these titrations.

[LCH]

20 Environmental Chemistry

OBJECTIVES

- To give students an understanding of sources of water contamination and its consequences.
- To give students an appreciation of the importance of providing clean water for human use.
- To give students an understanding of the consequences of the natural greenhouse effect and the enhanced greenhouse effect.

20.1 Introduction

Water is one of the most abundant and most important chemicals on Earth. About 80% of the Earth's surface is covered with water and it makes up about two-thirds of our body mass. Water is essential for life. We could survive for several weeks without food, but we could not live for more than a few days without water. In fact, we need to take in about two litres of water every day in order to stay healthy.

One of the most important properties of water is that it is an excellent solvent. Each day we use large quantities of water for various purposes – drinking, washing, flushing the toilet and watering the garden. Industry uses vast quantities of water for cooling, manufacturing various products and generating electricity. We take water very much for granted and yet it is one of the most important items that we require. In the first part of this chapter, we will study the importance of water in our environment. In the second part of the chapter, we will continue our studies of the environment by taking a close look at the greenhouse effect.

20.2 Water – A finite resource

You may recall in studying science at Junior Cycle that you learned about the way in which water circulates around the Earth. This may be represented by the water cycle, Figure 20.1.

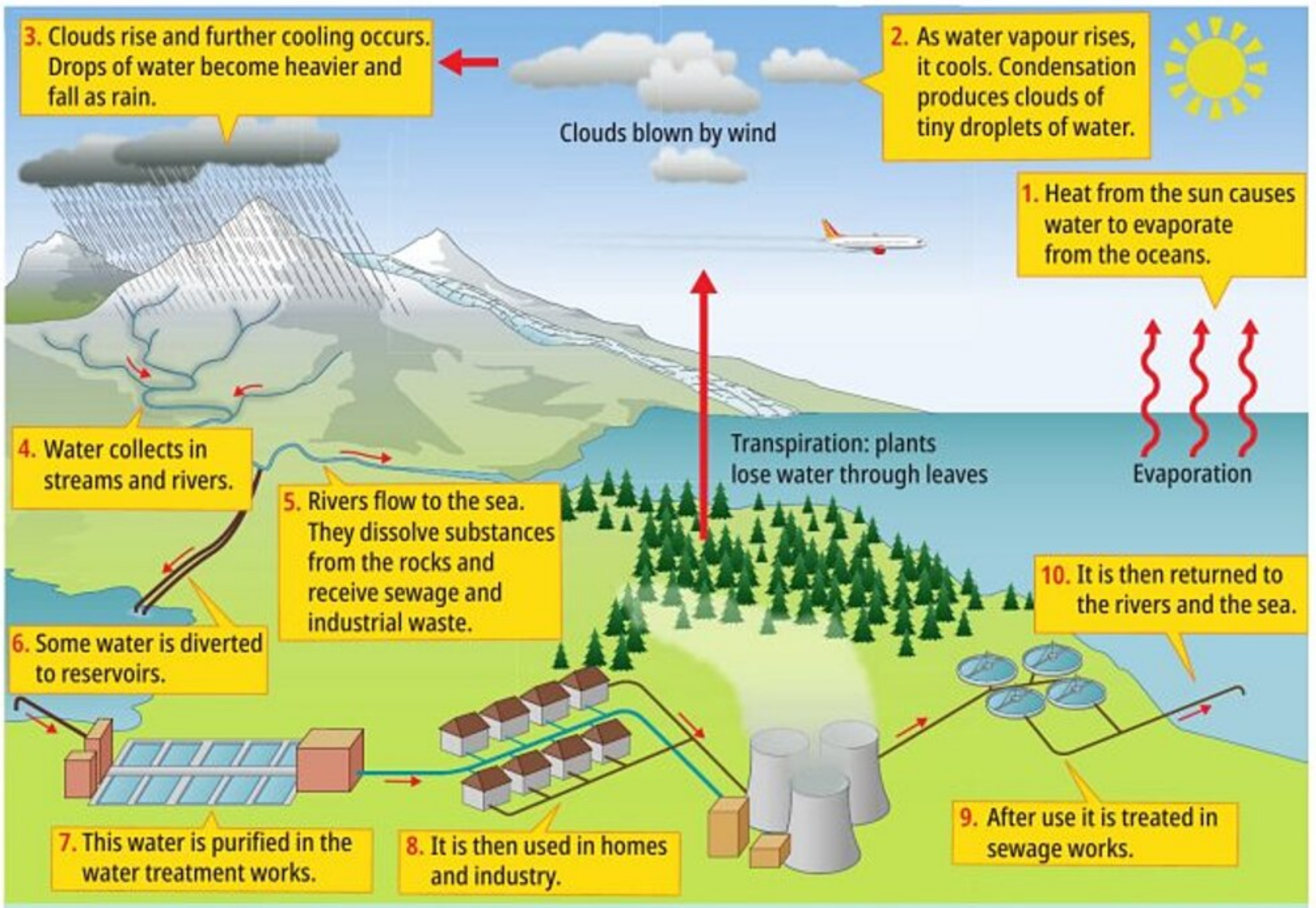

3. Clouds rise and further cooling occurs. Drops of water become heavier and fall as rain.
Clouds blown by wind
2. As water vapour rises, it cools. Condensation produces clouds of tiny droplets of water.
1. Heat from the sun causes water to evaporate from the oceans.
Transpiration: plants lose water through leaves
Evaporation
4. Water collects in streams and rivers.
5. Rivers flow to the sea. They dissolve substances from the rocks and receive sewage and industrial waste.
10. It is then returned to the rivers and the sea.
6. Some water is diverted to reservoirs.
7. This water is purified in the water treatment works.
8. It is then used in homes and industry.
9. After use it is treated in sewage works.

Figure 20.1 The water cycle represents the way that water circulates through the oceans, atmosphere and Earth.

As you can see from the water cycle, it seems that water is everywhere – in the oceans, clouds, rivers and underground. However, you may be surprised to learn that:

- About 97% of all the water on Earth is saltwater. This is not of much use to us for drinking without spending a lot of money to remove the dissolved salts.
- Of the remaining 3% of water (which is freshwater), about two-thirds of this water is locked away in glaciers and ice caps or is deep underground.
- Only about 1% of all water on Earth is easily accessible in our rivers and lakes and in groundwater near the surface of the earth.

Therefore, water is often referred to as a **finite** or **limited** resource, since there is a limited amount of water that is available to us on Earth. Even though water is being recycled as shown in Figure 20.1, the total amount of freshwater available to us does not increase. As the population of the world increases, the demand for clean water rises. It would be of some help if the supply of available freshwater stayed the same. Unfortunately, the supply is actually decreasing due to increasing levels of contamination.

20.3 Causes of water contamination

Water contamination is the introduction of substances into water that makes it unsafe for consumption or harmful to ecosystems.

Water contamination may be defined as follows:

The six causes of water contamination that are on our course are summarised in Table 20.1.

	Cause	Chemistry involved	Biochemical consequences
1.	Sewage	This contains high levels of organic matter, e.g. carbohydrates, proteins, fats and urea.	Levels of oxygen dissolved in water are decreased by bacterial decomposition. Biochemical Oxygen Demand (explained later) is increased resulting in fish kills.
2.	Industrial effluent	This could contain organic solvents or toxic chemicals.	Toxic substances can accumulate in food chains and damage organs in aquatic life. This can also alter pH and temperature of water and harm ecosystems.
3.	Agricultural effluent	Runoff water from farms may contain nitrates and phosphates from fertilisers, and also may contain pesticides.	Nitrates and phosphates act as nutrients and cause excessive growth of algae (algal bloom). Decomposition of algae causes eutrophication (explained later). Pesticides can be toxic to aquatic life.
4.	Microplastics	These are tiny plastic particles (< 5 mm) whose chemical composition is harmful to health. They can transport toxins.	These are ingested by aquatic organisms, who mistake them for food. Microplastics can kill organisms and can be transferred up the food chain to affect human health.
5.	Heavy metals	These are metals such as mercury, lead and cadmium. They can end up in water through improper disposal of batteries, electronic waste, industrial waste and mining.	Heavy metals interfere with the actions of enzymes in the human body and can cause damage to the kidneys and liver. They can also cause neurological damage. Pb^{2+} ions mimic Ca^{2+} ions, interfering with the functioning of nerves and bone development as well as causing brain damage, especially in children.
6.	Acidification	Acid rain or acidic industrial discharges can lower the pH of water.	Acidic conditions interfere with enzyme function and damage tissues. Organisms such as shellfish are badly affected, as the acid destroys their protective shells. Acidification can also release toxic metals from compounds.

Table 20.1 Summary of the main causes of water contamination

Note the term *biochemical consequences* used as a heading in the table above. Biochemical consequences of water contamination refer to the chemical and biological effect that contaminants have on living organisms and on the environment. In other words, the biochemical consequences of chemical changes in the water result in the harming or killing of living things.Let us now discuss in more detail the concept of Biochemical Oxygen Demand in point 1 of Table 20.1.

Biochemical Oxygen Demand

Dissolved oxygen is often referred to as 'the breath of life under water'. Dissolved oxygen in rivers, lakes and the sea is vital for the survival of fish and other forms of life, Figure 20.2.

- Since the O_2 molecule is nonpolar, the solubility of oxygen in water (a polar solvent) is quite low and depends on the temperature of the water. For example, at 10 °C the solubility of oxygen is 11.3 mg/L (ppm) whereas at 20 °C the solubility of oxygen drops to 9.2 mg/L. (The fact that solubility of gases in water drops with increase in temperature is observed when water is heated. As the water is heated, bubbles of air are seen to come out of solution.)

Now consider what happens when organic waste is discharged into a waterway. Examples of organic waste are domestic sewage, animal slurry, silage effluent from farms, effluents from food processing factories, milk and industrial waste. When the organic waste is discharged into the water, the bacteria and other organisms that are naturally present in the water are provided with nutrients. These nutrients cause the organisms to multiply into large numbers. As the organisms break down the waste into compounds such as carbon dioxide and water, they use up the oxygen dissolved in the water.

organic matter + oxygen → carbon dioxide + water

- If a considerable amount of organic waste is present, it is possible that the dissolved oxygen level in the water will be reduced so much that fish life in the water may be reduced or possibly killed off completely. For example, trout and salmon need an approximate concentration of 5 ppm of dissolved oxygen in order to survive.
- The dissolved oxygen used up by bacteria may not be replaced fast enough by more oxygen from the air dissolving in the water.

Figure 20.2 Fish absorb dissolved oxygen from the water through their gills. The air pump produces bubbles that stir the water and help fresh air to mix with the water so that oxygen levels are maintained.

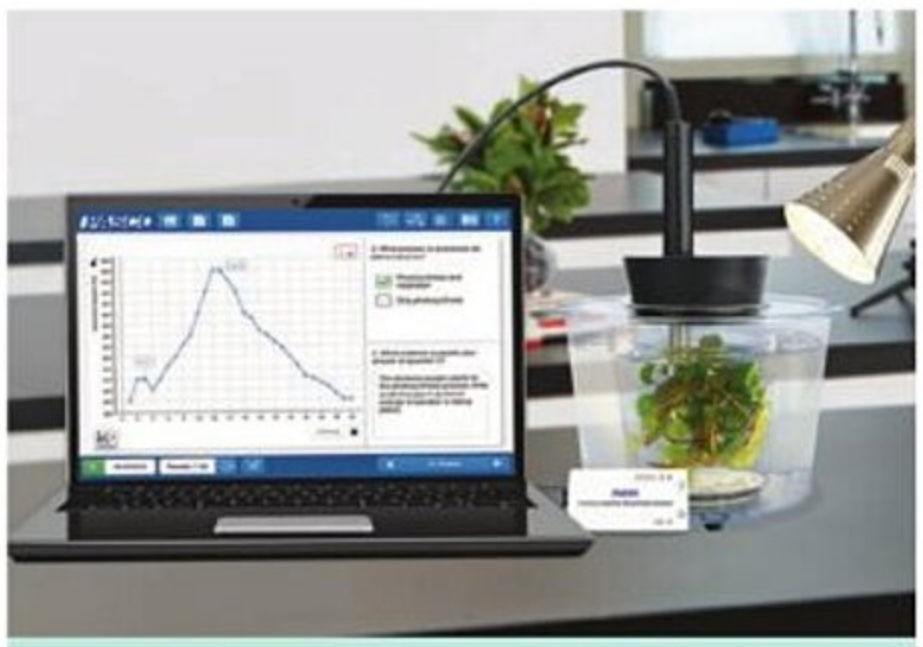


Figure 20.3 This dissolved oxygen sensor measures the concentration of dissolved oxygen in the water.

- If the dissolved oxygen drops to zero concentration, anaerobic bacteria (bacteria that do not require oxygen) will take over and the river will become foul-smelling due to the presence of hydrogen sulfide gas, H_2S.

The concentration of dissolved oxygen is measured using a dissolved oxygen sensor, Figure 20.3.

The release of substances into the environment that damage the environment is called **pollution**. In the early 1900s, the Royal Commission on Sewage Disposal introduced a test to measure the demand that water has for dissolved oxygen. This test is called the **Biochemical Oxygen Demand** test or, more simply, the B.O.D. test. It is simply a method used by chemists to indicate the level of pollution in a sample of water.

The main points about the B.O.D. test may be summarised as follows:

- The B.O.D. test is carried out by **completely** filling two bottles with the water to be tested.
- The measurement of dissolved oxygen is carried out immediately in one of the bottles so that the oxygen content does not increase due to photosynthesis by plant material in the water or decrease due to respiration by microorganisms in the water.
- The second bottle is incubated at 20 °C in darkness for five days, Figure 20.4.
- The second bottle is kept in darkness to prevent photosynthesis taking place, as this would increase the level of oxygen in the water.
- The purpose of the fixed temperature of 20 °C is because a fixed temperature is required for a valid comparison of different water samples as the amount of oxygen dissolved in water depends on temperature. Also, the rate at which oxygen is consumed by microorganisms depends on temperature.
- When the five-day period has elapsed, the amount of dissolved oxygen remaining in the second bottle is measured.
- The B.O.D. is the difference in the two dissolved oxygen levels, as this is the amount of oxygen that has been used up during the test. B.O.D. is measured in mg/L (ppm) of oxygen.

Examples of B.O.D. values are given in Table 20.2. Note that the higher the B.O.D. is, the more polluted the water. A high B.O.D. value means that there is a large amount of organic waste in the water and, as this organic waste is acted on by bacteria, the level of oxygen becomes depleted.

Biochemical oxygen demand (B.O.D.) is defined as:

- The amount of dissolved oxygen
- Consumed by biological (biochemical) action
- When a sample of water is kept at 20 °C
- In the dark
- For five days.

Figure 20.4 Two samples of water are needed to calculate the B.O.D. of a water sample.

B.O.D. (mg/L)	Example
1–2	Clean water
20–40	Treated sewage
100	Polluted water (fish die)
300	Raw sewage
500	Brewery effluent
30000	Pig slurry
54000	Silage effluent

Table 20.2 Some examples of B.O.D. values

Most of the fish kills in Ireland are caused by silage and slurry effluent being discharged into rivers and lakes.

The B.O.D. test may be used to measure the level of pollution in effluents. However, because of the low solubility of oxygen in water (9.2 mg/L at 20 °C), water samples with B.O.D. values greater than 9 mg/L must be diluted by a fixed amount with well-oxygenated, pure water. This is done in order to ensure that dissolved oxygen will be present throughout the five-day period of the test and that a measurable amount of oxygen (at least 2 ppm) will be left after the five-day period. Fresh distilled water is used for diluting the sample and the mixture must be well-shaken for a few minutes in order to oxygenate the water fully. If the effluent is not diluted, it is possible that all of the oxygen will be used up before the five days have elapsed.

Since B.O.D levels about 9.2 mg/L are not actually possible (as this is the maximum concentration of dissolved oxygen at 20 °C), values greater than this are generated when the figure obtained in the experiment is multiplied by an associated dilution factor.

Let us now discuss the concept of eutrophication mentioned in point 3 of Table 20.1.

Eutrophication

The level of dissolved oxygen in water may also be reduced if the water is overloaded with plant nutrients, especially nitrate ions (NO_3^-) and phosphate ions (PO_4^{3-}).

This 'over-enrichment' is called **eutrophication** (a Greek word meaning 'well nourished').

Eutrophication is the enrichment of water with nutrients, leading to excessive growth of algae and other plants.

The main points about eutrophication may be summarised as follows:

- Eutrophication may occur naturally or artificially.
- Natural eutrophication occurs mainly in lakes and is caused by a gradual increase in nitrogen and phosphorus levels caused by sediments building up in these lakes.
- Artificial eutrophication is caused by a sudden increase in nitrate and phosphate nutrients resulting from artificial fertilisers being washed into rivers and lakes, or by domestic sewage or waste from intensive farming entering these waterways.
- As the nitrate and phosphate levels rise, they are absorbed by plants and many of these plants and floating algae undergo rapid growth.
- The rapid growth gives rise to algal blooms that cover much of the surface of the water with a green scum, Figure 20.5.
- The algae are short-lived and when they decay a heavy oxygen demand is placed on the water due to increased activity by microorganisms.
- This increased activity causes the dissolved oxygen level to fall and many forms of animal life in the water are killed.

Figure 20.5 Algal bloom is caused by eutrophication.

There is some concern about the levels of nitrate ions in water. It is thought that high levels of nitrates may cause stomach cancer and also infant deaths.

We now discuss microplastics as mentioned in point 4 of Table 20.1

Microplastics

The main points about microplastics may be summarised as follows:

- Microplastics are tiny plastic particles of size less than 5 mm. This term is used to distinguish them from larger plastic waste.
- They are dangerous to human health as many plastics contain harmful chemicals which can end up in water and food.
- Since microplastics are so small, they can be eaten by fish and other aquatic organisms. Therefore, they can enter the food chain and cause damage to human health.
- Microplastics come from a variety of sources, e.g. cosmetics, personal care products, synthetic clothing (such as polyester and nylon) and food packaging, Figure 20.6. Although waste from our homes is treated in wastewater (sewage) treatment plants, not all microplastics are removed in these treatment plants and so they enter rivers, lakes and oceans.
- Microplastics can also enter rivers, lakes and oceans from runoff water from roads, e.g. tyres are made from synthetic rubber and this releases microplastics. These particles accumulate on roads and are washed into the storm-water drainage system, which carries the untreated water into rivers, lakes and oceans.
- We will see later how water for drinking-water treatment plants is taken from rivers and lakes. Since microplastics are so small, it is possible that not all microplastics are removed in the drinking-water treatment process and, therefore, could end up in tap water in our homes.
- It is also possible for microplastics to enter the drinking water supply from plastic pipes in the water distribution system. Plastic pipes (e.g. PVC) can degrade over time, especially if they contain water under pressure.
- **Primary microplastics** are intentionally manufactured to be very small, for example, the tiny plastic beads shown in Figure 20.6. **Secondary microplastics** are formed when larger plastics (e.g. plastic bags) break down.
- Microplastics are known to persist in the environment at high levels, e.g. rivers, oceans and in soil.
- One of the big problems about microplastics is that, like all plastics, they degrade very slowly and can take hundreds or thousands of years to fully degrade.

Let us now take a look at heavy metals mentioned in point 5 of Table 20.1.

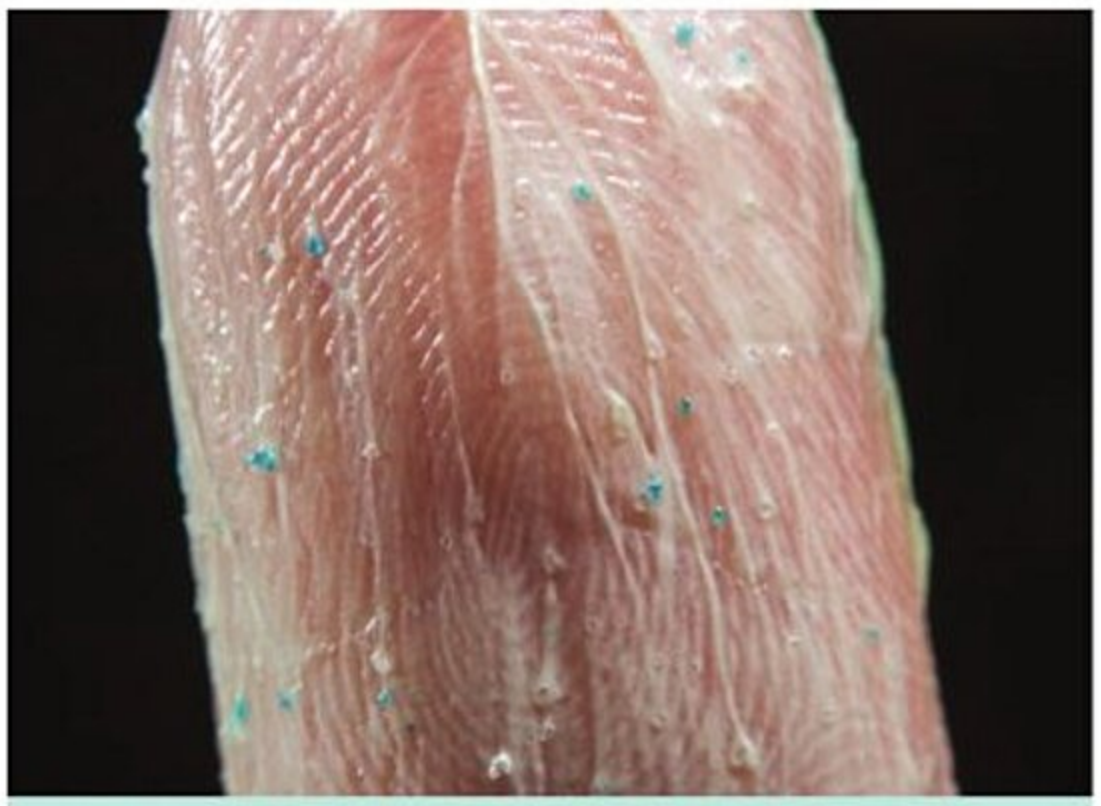


Figure 20.6 These microplastics came from an exfoliating skin scrub and are so small that many of them fit on the tip of a finger.

Heavy metals

Heavy metals are elements with high relative atomic mass. Heavy metals which are toxic include lead (Pb), mercury (Hg) and cadmium (Cd). The following is a summary of the main points about heavy metals:

- Water can be polluted by the release of toxic metal ions into the water, e.g. lead ions (Pb^{2+}), mercury ions (Hg^{2+}) and cadmium ions (Cd^{2+}). Hence, it is very important that these metals are disposed of in a proper manner, Figure 20.7.
- Due to the high relative atomic masses of the metals, these ions are commonly referred to as 'heavy metal ions'.
- Lead, mercury and cadmium are often classified as cumulative poisons, i.e. their concentrations tend to build up in the body upon continual exposure. They cause brain damage as well as harming the kidney, liver and bones.
- These metals could possibly be found in rivers and lakes as a result of the discharge of industrial effluents (e.g. during battery production), mining or, in the absence of recycling, the dumping of batteries that contain these metals.
- Lead in drinking water is a problem in very old houses containing lead plumbing. (The word 'plumbing' comes from the Latin word *plumbum*, meaning lead).
- Lead is a poisonous substance and is particularly harmful to young children, who can suffer brain damage if exposed to lead compounds over a period of time.

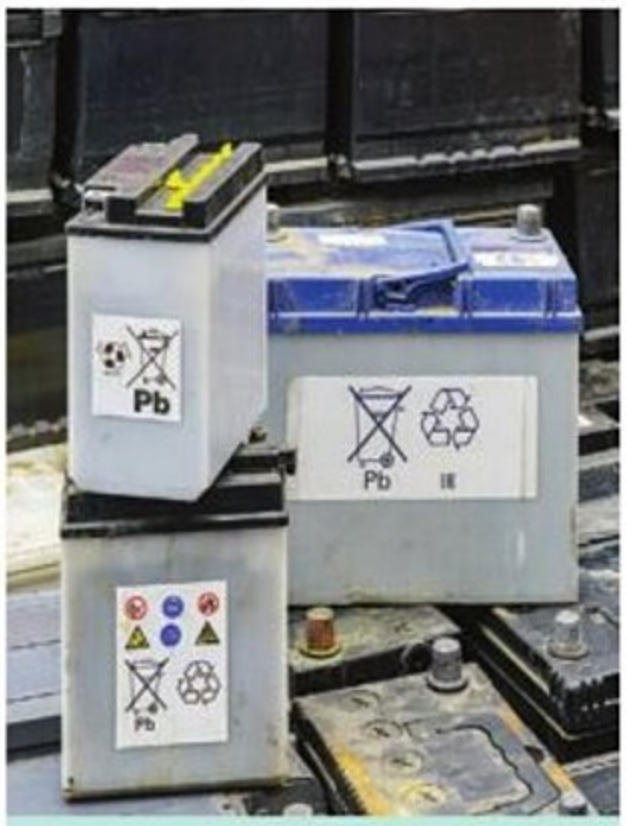


Figure 20.7 These batteries contain lead and must be recycled to avoid pollution from Pb^{2+} ions.

The best-known case of mercury poisoning occurred in Minamata Bay, Japan in the late 1950s, Figure 20.8.

Industrial waste containing mercury salts was discharged into Minamata Bay. The mercury salts became incorporated into the food chain and high levels of mercury were found in fish that were consumed by the local population. The mercury caused birth defects and deaths and the disease caused by the mercury poisoning became known as Minamata disease. Nowadays, the mercury is recovered from industrial waste before it is discharged into water.

Finally, let's have a closer look at the contamination of water as a result of acidification, as mentioned in point 6 of Table 20.1.

Figure 20.8 Mercury salts were discharged into Minamata Bay in Japan. The high levels of mercury in fish consumed caused many deaths and birth defects in the local population.

Acidification

The main points about acidification may be summarised as follows:

- The main source of acidification is caused by acid rain and acidic industrial discharges directly into waterways, Figure 20.9.
- The acidic water can dissolve metals such as Al^{3+} ions and heavy metals from rocks and sediments. These metals damage fish gills and cause fish kills.
- The change in pH affects aquatic life, since many species cannot survive at pH lower than 5. The low pH interferes with enzyme activity, salt balance and ion transport in cells.
- Organisms such as shellfish and snails are badly affected, as the acid destroys their protective shells.
- In general, there is a decline in biodiversity as many species are unable to survive at the lower pH.

TEST YOURSELF: Attempt Questions 20.1–20.3 and W20.1–W20.3.

Figure 20.9 Acid rain is one of the sources of acidification of water.

20.4 Water treatment

It has been estimated that each household in Ireland uses about 300 litres of water each day. The water supplied to each of our houses by Uisce Éireann around the country must fulfil certain criteria. It must be attractive looking (i.e. colourless), it must be odourless, it must be safe to drink (no active bacteria present) and it must be fluoridated. In order to ensure that the quality of domestic water supplies is of an adequate standard, it is necessary to carry out certain procedures on the water taken from a river or lake. Water treatment plants have been set up throughout the country. The various stages in the process of water treatment may be summarised as follows:

1. Screening

- The water (usually taken from a river or lake) is passed through a wire mesh to remove any floating debris such as twigs, leaves and plastic bags.

2. Flocculation

The water that comes directly from the river or lake is often called 'raw' water because it is unsafe to drink. It may be cloudy due to the presence of suspended particles in the water. The second stage involves the removal of these suspended particles from the water.

- The word 'flocculation' means coagulation. It comes from a Latin word *floccus*, meaning tuft or clump – like a tiny piece of cotton wool.
- Very small suspended solids in the water can be made to form larger particles (called 'flocs') by adding certain chemicals to the water. This process is called flocculation.
- Chemicals that bring about flocculation are called **flocculating agents**.
- The most commonly used flocculating agent is aluminium sulfate, $Al_2(SO_4)_3$. The addition of aluminium sulfate to the water causes the suspended solids to coagulate or stick together, Figure 20.10.
- The amount of aluminium sulfate added to the water must be controlled, as excess aluminium sulfate affects the taste of water and causes corrosion of pipes.
- Tiny particles suspended in the water may be too small to settle out of the water on their own. Therefore, the water may look cloudy. Flocculating agents cause these to clump together and make them easier to remove by sedimentation or filtration.
- The flocs fall to the bottom of the tank in which flocculation takes place. The sludge formed is pumped out of the tanks and treated elsewhere.

Figure 20.10 Aluminium sulfate is a flocculating agent and is added to water to coagulate suspended particles in the water.

Flocculation is the coming together (coagulating or clumping) of small, suspended particles in water into larger particles.

A **flocculating agent** is a chemical added to water to coagulate suspended particles and thus help sedimentation to take place.

3. Sedimentation (also called settling)

- The water is now passed into large settling tanks. The water flows in at the bottom of these large tanks and rises up slowly to the surface where the clear water is allowed to overflow (decant) into channels, Figure 20.11.
- The water is allowed to rise up towards the surface very slowly to allow maximum settlement to take place at the bottom of the tank due to gravity. Heavier particles sink faster than lighter ones.
- Over 90% of the suspended particles are removed in the sedimentation stage. If these particles were not removed, the water would look cloudy. Removing the large particles at the beginning of the treatment process is important, as it makes later steps such as filtration more efficient and less costly.
- This process is entirely physical, i.e. no chemicals are added at this stage.
- The substance formed at the bottom of the tank is called sludge. This sludge contains decaying vegetation, leaves, algae and clay. The sludge is pumped out of the tanks and treated elsewhere.

Figure 20.11 Settling tanks at Inniscarra Water Treatment Plant, Co. Cork.

Note: As a result of increased demand for water in recent years, modern water treatment plants do not have the capacity to store vast quantities of water. Therefore, flocculation is carried out **before** sedimentation as described above. If you visit an old water treatment plant, you may find that steps 2 and 3 are in reverse order.

4. Filtration (sand and microfiltration membranes)

- In the next stage, the water is then passed through large beds of sand to physically remove suspended solids by filtration, Figure 20.12. You may recall the process of filtration from your study of Junior Cycle science.

Filtration is a method of separating an insoluble solid from a liquid using a material that allows the liquid to pass through, but not the solid.

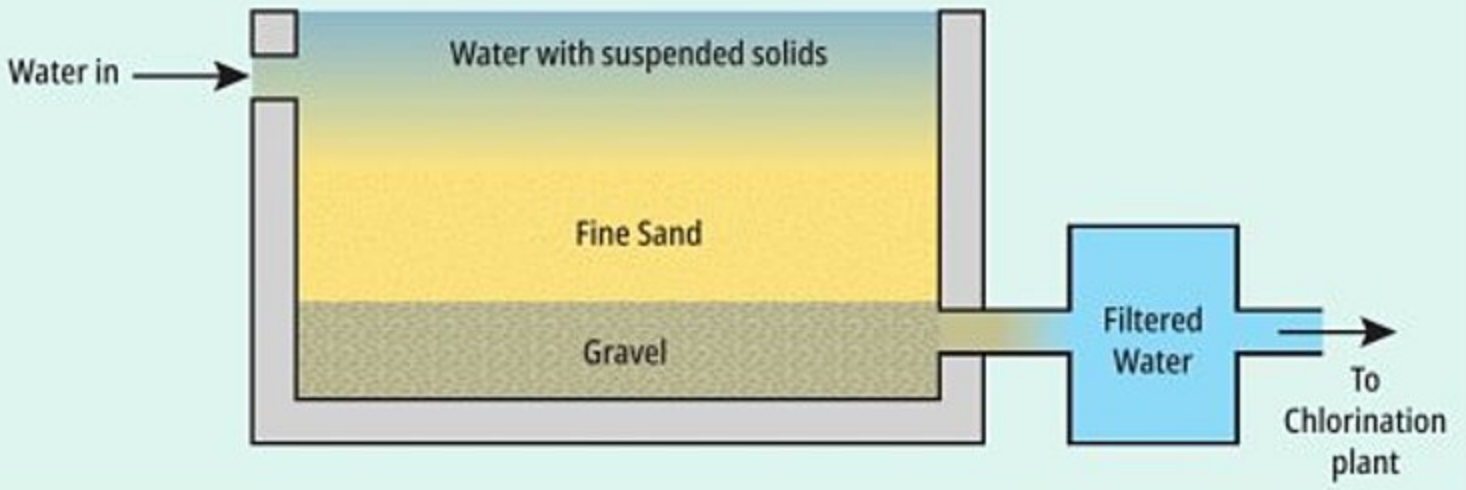


Figure 20.12 Any remaining suspended solids are removed by filtration. The diagram shows sand filtration in operation.

These filter beds remove any remaining suspended solids. In **sand filtration**, water is passed through layers of coarse and fine sand. As water flows through the layers of sand, the suspended particles get trapped in the spaces between the grains of sand. Thus, the sand acts just like a sieve or filter paper to remove the suspended solids. The sand is supported on a layer of gravel and the layers of sand are cleaned regularly. Some filtration tanks are shown in Figure 20.13.

In some water treatment plants, a process called **microfiltration** is carried out. This is similar to sand filtration except that a plastic membrane with tiny pores is used. The tiny pores are usually between 0.1 and 10 micrometres (10^{-6} m) in diameter. A micro metre (μm) is one-millionth of a metre. Microfilters are made from strong durable plastic materials called polymers (Chapter 24).

Water is forced through the membrane under pressure. The pores are so small that not only are suspended solids removed, but also bacteria are removed. However, it does not remove viruses since these are small enough to get through the pores.

- The water that comes out of the filter beds is now clear. However, it is not fit to drink as it may still contain harmful bacteria (if only a sand filter is used) or viruses. This problem is dealt with in the next stage.
- Note that at this stage, suspended solids have been removed by three methods: (i) sedimentation (settling), (ii) flocculation and (iii) filtration.

Figure 20.13 These large filtration tanks contain filter beds of sand that remove any remaining suspended solids.

5. Chlorination

- This step is an important disinfection step. Chlorine is added to the water in order to sterilise it, i.e. to kill any harmful microorganisms in the water.

  Chlorine reacts with water to form an acid called hypochlorous acid. This acid kills the microbes.

$$Cl_2 + H_2O \rightarrow \underset{\text{hypochlorous acid}}{HOCl} + HCl$$

- The chlorine need only be present in small quantities (approximately 0.5 ppm). If too much chlorine is added, it gives the water an unpleasant taste and smell. The amount of chlorine gas added to the water is carefully controlled, Figure 20.14. Sufficient chlorine must remain in the water to ensure that the water is kept safe for drinking when it is being distributed to our homes. Water can get contaminated in pipes or reservoirs. The amount of chlorine still present in the water is called the **chlorine residual**. This residual is important to ensure ongoing disinfection while the water is being stored or distributed.
- The effectiveness of the chlorine treatment is continually monitored by examining the water for the presence of microorganisms in the water.

Figure 20.14 The chlorine gas in these cylinders is injected continuously into the water to kill bacteria.

6. Fluoridation

- By law, all water treatment plants in Ireland must include fluoridation as part of the water treatment process. This involves adding small quantities (about 1 ppm) of fluorine compounds to the water.
- Examples of fluorine compounds commonly added are sodium fluoride, NaF, and hexafluorosilicic acid, H_2SiF_6.
- Water is fluoridated because it has been shown that the presence of fluoride ions in water helps to reduce tooth decay. It does this by strengthening the enamel of teeth.
- The level of fluoridation is carefully controlled in the water treatment plant as excess fluoride in water gives rise to a condition known as fluorosis which causes staining of teeth, Figure 20.15.

Figure 20.15 In some parts of the world there is an excess of fluoride ions found naturally occurring in the water supply, and this causes teeth to be stained. This condition is known as fluorosis. These photos show the teeth of a person with fluorosis, before and after treatment.

7. pH Adjustment

pH sensors are used in the laboratories of water treatment plants in order to monitor the pH of water taken from rivers and lakes.

- Water coming from limestone areas tends to be basic with a pH of about 7.8. Water coming from sandstone areas and bogs tends to be acidic and could have a pH as low as 5.8.
- The optimum pH of water for distribution to homes and factories is about 7.2. Therefore, Uisce Éireann has to alter the pH of the water before distributing it to homes and factories.
- If the water supply is slightly acidic, it may cause corrosion of pipes. Therefore, the pH has to be raised above 7 and a substance such as **calcium hydroxide** (lime) is commonly used for this. The amount of calcium hydroxide added must be controlled, as adding too much could affect the taste of the water.

- If the water contains high levels of Ca^{2+} or Mg^{2+} ions ('hard' water), Uisce Éireann may soften it by adding in substances such as sodium carbonate (a base). If this causes the pH to be too high, it is lowered using dilute **sulfuric acid** or carbon dioxide. Care has to be taken to avoid adding excess sulfuric acid, as this could cause corrosion in pipes.

A summary of the chemicals added to water during the treatment process is given in Table 20.3.

Name of chemical	Purpose	Problems caused by adding excess
Aluminium sulfate	Coagulation of small suspended particles	Taste of water affected; corrosion of pipes
Chlorine	Sterilise water (kill harmful microorganisms)	Taste and smell of water affected
Fluorine compound (e.g. sodium fluoride or hexafluorosilicic acid)	Reduce tooth decay	Staining of teeth
Calcium hydroxide	Raise pH	Hardness of water
Sodium carbonate	Soften water	Taste of water affected
Sulfuric acid	Lower pH	Corrosion of pipes

Table 20.3 Summary of chemicals used in water treatment

8. Ultraviolet (UV) treatment

When discussing the use of chlorine in water treatment plants, we saw that chlorine was used to disinfect water. In some water treatment plants, ultraviolet (UV) radiation is used as a final disinfection step. UV treatment involves exposing water to UV radiation of a specific wavelength to kill microorganisms in the water. It is often used in addition to chlorination rather than as a complete replacement. Some of the advantages and disadvantages of UV treatment compared to chlorination are given in Table 20.4.

Advantages of UV treatment	Disadvantages of UV treatment
• Does not use any chemicals, so it is more environmentally friendly. No need to transport, handle or store hazardous, toxic chlorine.	• UV lamps have high maintenance (contain mercury), consume electricity and need regular cleaning and replacement.
• No chlorine residual in the water.	• If there are any suspended particles in the water, these can shield the microorganisms from UV light.
• It kills some organisms such as cryptosporidium, which are resistant to chlorine.	• It has been found that some microorganisms can repair and reverse the destructive effects of UV radiation.

Table 20.4 Comparing some advantages of UV treatment relative to chlorine, with some disadvantages of UV treatment of water.

The treated water that leaves the treatment plant is then stored in reservoirs for distribution throughout the water supply network.

Energy and environmental impact of water treatment

As already discussed, access to clean, safe drinking water is essential for public health. However, it is important to bear in mind that there is a high cost to the water treatment process, which is summarised in Figure 20.16.

Therefore, we need to avoid wasting water and we need to use it as efficiently as possible. Energy must be used in the water treatment plant to produce drinking water for distribution to our homes. Some examples of how this energy is used are:

- Pumping water from rivers and lakes into the water treatment plant
- Pumping water through each stage of the process within the water treatment plant
- Stirring and mixing chemicals during the flocculation process
- Pumping sludge out of the flocculation tanks
- Cleaning sand filters and membrane filters using pressure pumps for water
- Operating all the equipment in the laboratories and administration buildings
- Pumping water over long distances from the water treatment plant throughout the water supply network – often against the force of gravity.

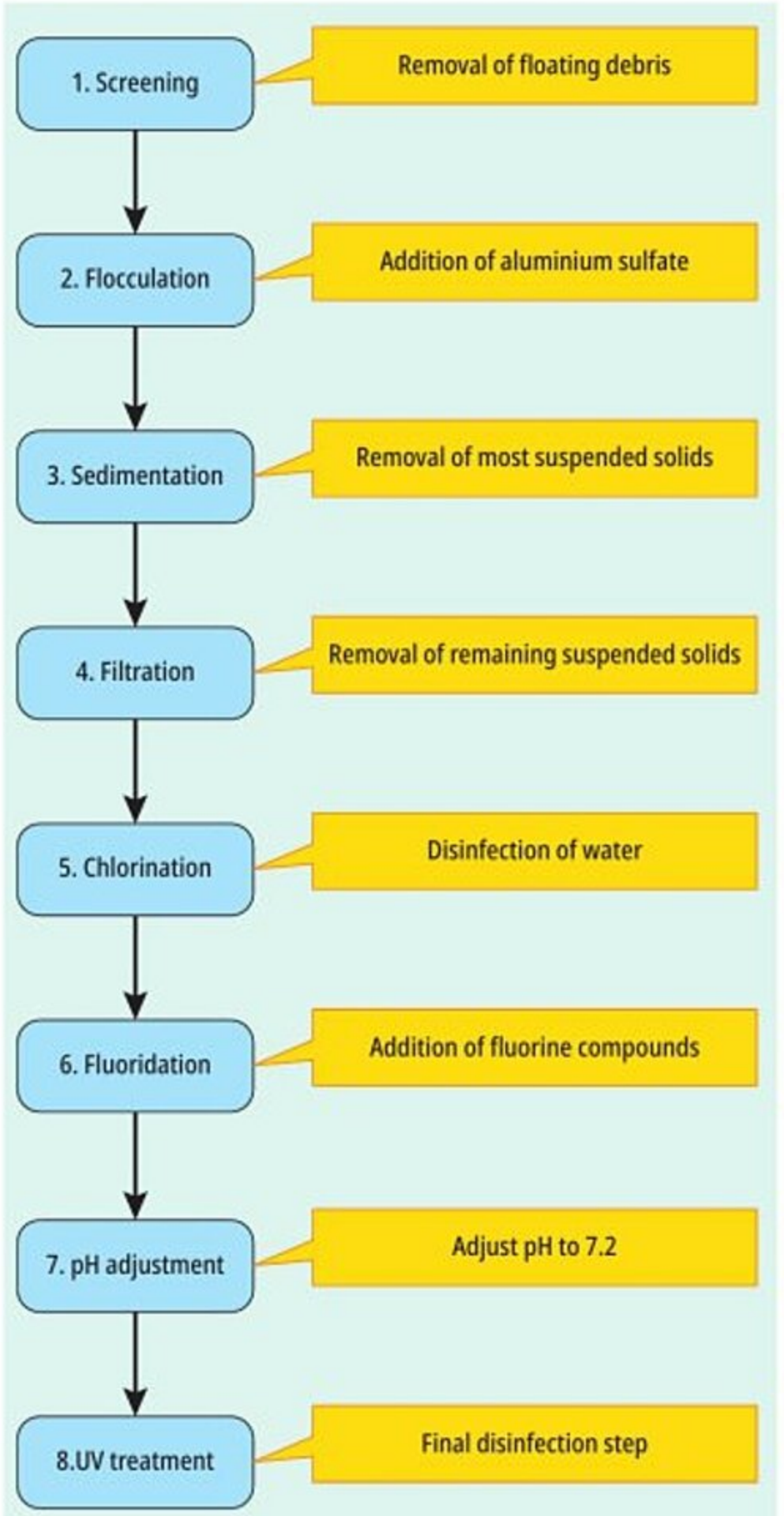


Figure 20.16 Summary of stages in treatment of drinking water

Positive environmental impacts of safe drinking water production

- Public health, e.g. waterborne diseases such as cholera and typhoid are eliminated in the water treatment process.
- The availability of tap water means that we do not have to rely on bottled water. This lowers plastic waste and transportation costs and pollution caused by this transportation.

Negative environmental impacts of safe drinking water production

- Energy consumption (as described above).
- Chemical usage: the production and transport of these chemicals has an environmental impact, e.g. carbon dioxide emissions and use of resources to manufacture chemicals.
- Generation of sludge in the sedimentation and flocculation stages – this needs to be disposed of properly.
- Wastewater from washing sand filters and membrane filters.

Modern water treatment plants have introduced sustainable practices to reduce environmental impact. These are summarised in Table 20.5.

Feature	Traditional treatment plant	Modern treatment plant
Energy	Energy from burning fossil fuels	Renewable energy – solar energy and wind energy are used to generate electricity.
Disinfection	Chlorination	UV disinfection takes place.
Sludge handling	Sent to landfill	Sludge is dried out and is used for making bricks. It is also added to soil as compost.
Monitoring of efficiency	Manual monitoring using digital systems done periodically	Sensor technology and artificial intelligence systems provide real-time monitoring of plant efficiency and detection of leaks.
Times when pumps operating	Pumps in operation continuously	Pumping of the water from the river or lake is scheduled for times when renewable energy is available. Energy from solar and wind sources is stored in batteries to power pumps. When treatment plants are designed, there is maximum use of gravity to move water around the plant.

Table 20.5 Comparing traditional water treatment plants with more modern water treatment plants

For example, solar panels help to reduce emissions of carbon dioxide and hence reduce the carbon footprint of water treatment plants. The reason for this is because solar panels reduce the need for electricity generated from fossil fuels such as natural gas, oil and coal. The burning of these fossil fuels produces carbon dioxide, which is a greenhouse gas. (This topic will be discussed in more detail later on in this chapter.)

Solar panels convert sunlight directly into electricity. During this process, no fuels are burned and no carbon dioxide is released into the air.

Deionised and distilled water

Since deionised water is so easily and cheaply produced, its use is far more widespread than that of distilled water. However, there is a slight difference between deionised water and distilled water. Distilled water is the purest form of water as **all dissolved and suspended solids as well as dissolved gases have been removed from the water**. Deionised water is not as pure as distilled water as deionised water normally contains dissolved gases and non-ionic material. These non-ionic substances, which do not dissociate into ions when dissolved in water, are often organic material that may be dissolved in the water. For some specialised industries (e.g. the electronics industry) the water must not contain any organic materials as this affects the purity of the silicon chips being manufactured. Therefore, in recent years, resins have been developed that remove organic material from water as well as ions.

» **Study SEC exam question 20.1 and model answer in online resources.**

In the second part of this chapter, we will discuss the carbon cycle and greenhouse effect.

TEST YOURSELF: Attempt Questions 20.4–20.5 and W20.4–W20.6.

20.5 The carbon cycle

When studying Junior Cycle science, we learned that all living things contain carbon and that carbon plays an important role in our lives. Our body is constantly 'burning' compounds of carbon to keep us alive in the process of respiration. Every time we breathe, we exhale carbon dioxide.

We also learned that plants depend on carbon to stay alive. Plants take in carbon dioxide and make glucose and oxygen from it during the process of photosynthesis.

We also learned that the Earth is surrounded by a layer of gases called the atmosphere. This layer reaches up to 100 km above the surface of the Earth. Carbon is present in the atmosphere as carbon dioxide. Although the percentage of carbon dioxide in the air is only 0.04 per cent approximately, it plays a very important role in our climate.

Some methods by which carbon dioxide is added to the atmosphere by **carbon sources** are summarised in Figure 20.17.

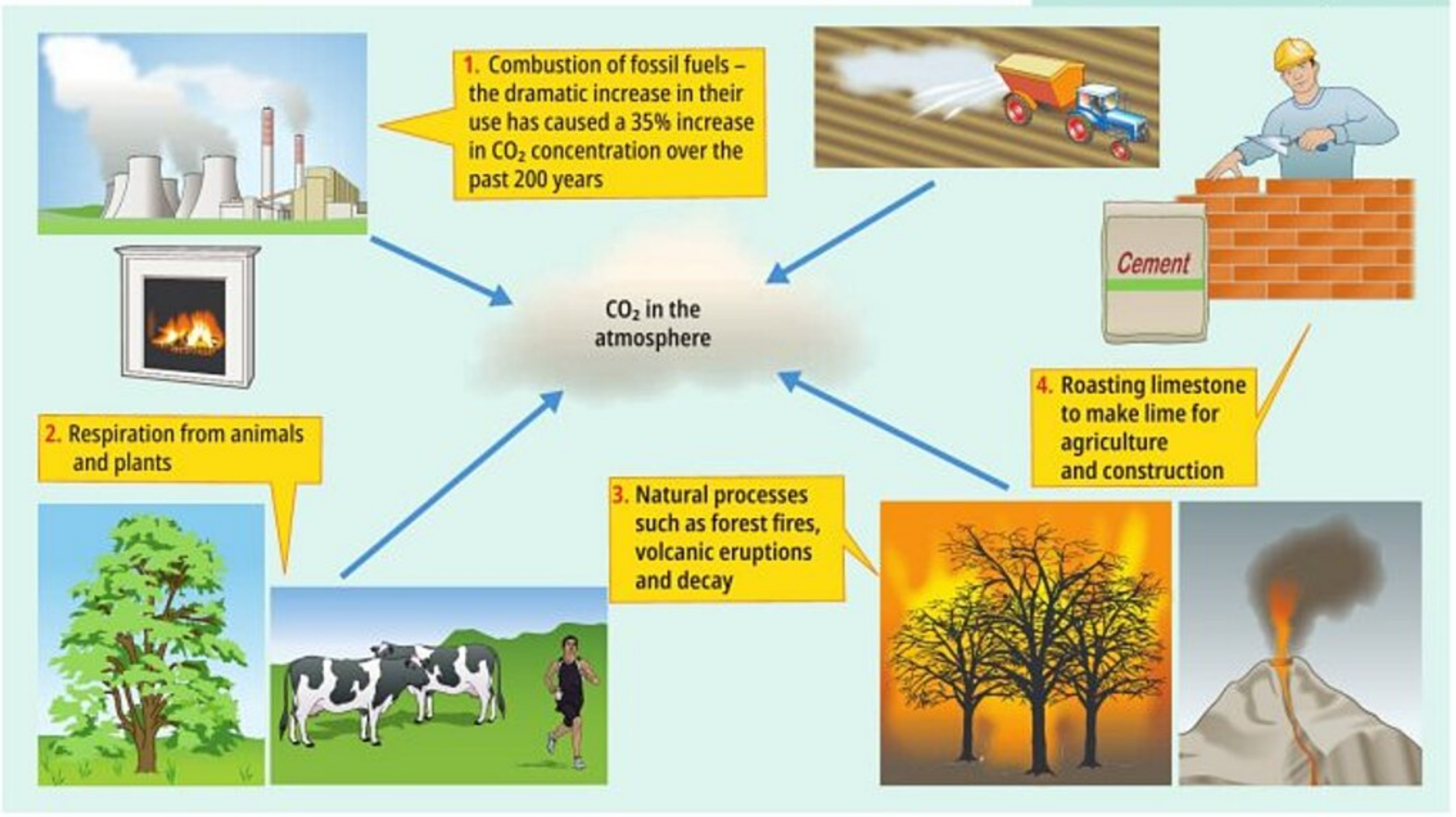

1. Combustion of fossil fuels – the dramatic increase in their use has caused a 35% increase in CO_2 concentration over the past 200 years
CO_2 in the atmosphere
Cement
2. Respiration from animals and plants
3. Natural processes such as forest fires, volcanic eruptions and decay
4. Roasting limestone to make lime for agriculture and construction

Figure 20.17 Summary of ways by which carbon dioxide is added to the atmosphere

Carbon dioxide is removed from the atmosphere by methods such as dissolving in water and by being used up in the process of photosynthesis, Figure 20.18. These systems are often called **carbon sinks**.

A **carbon sink** is a system that absorbs more carbon from the atmosphere than it releases.

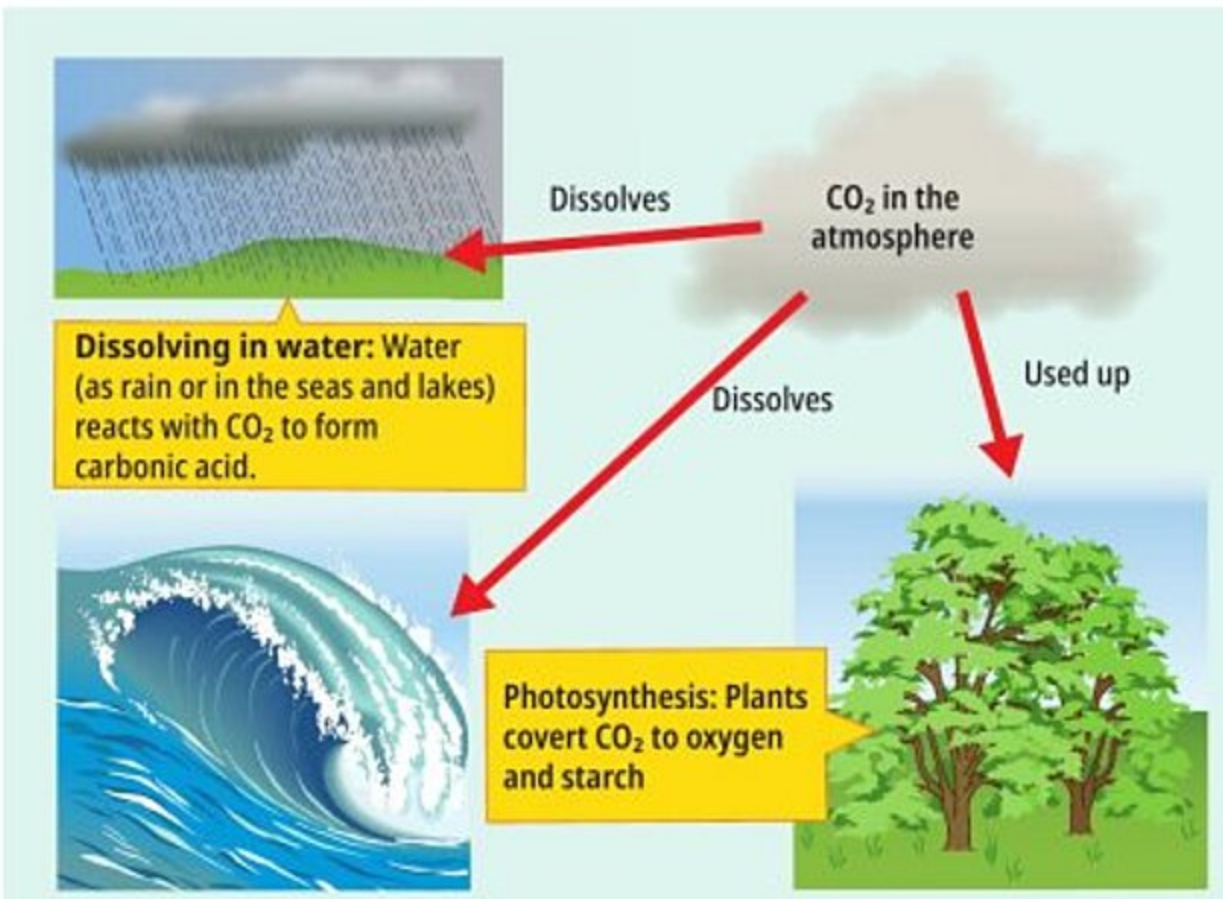

Dissolves
CO_2 in the atmosphere
Dissolves
Used up
Dissolving in water: Water (as rain or in the seas and lakes) reacts with CO_2 to form carbonic acid.
Photosynthesis: Plants covert CO_2 to oxygen and starch

Figure 20.18 Summary of ways in which carbon dioxide is removed from the atmosphere.

Comparing Figure 20.17 and Figure 20.18 we see that carbon sinks are the opposite to carbon sources.

As mentioned previously, the percentage of carbon dioxide in the atmosphere is fairly constant at 0.04% approximately. Studying the carbon cycle (Figure 20.19) will help you to understand why this is the case. The **carbon cycle** shows us how carbon (in carbon dioxide and other compounds) is recycled through various processes. Note that the left-hand side of the diagram summarises the carbon sources. The right-hand side of the diagram summarises the carbon sinks.

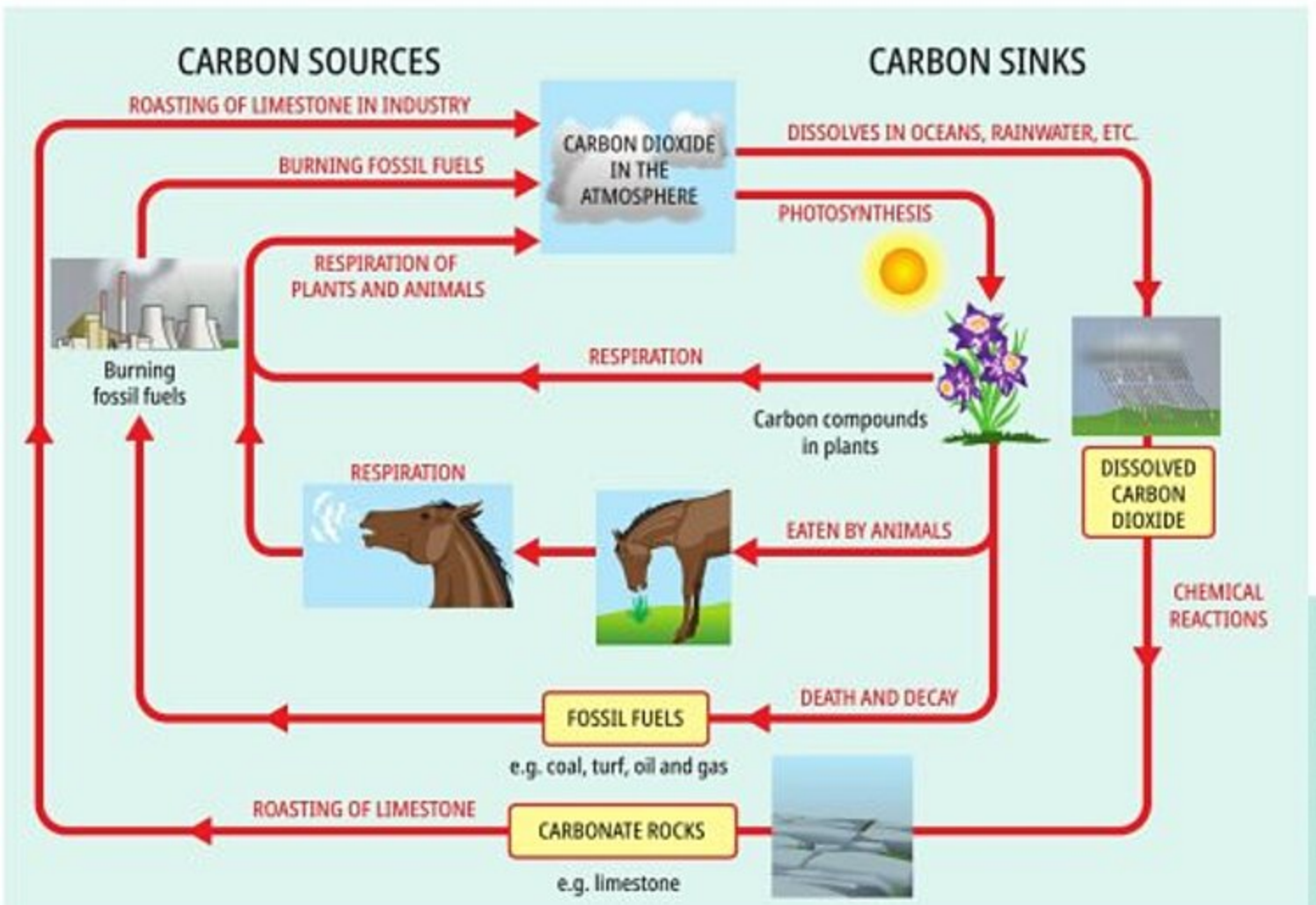


Figure 20.19 The carbon cycle describes the process in which carbon continuously travels from the atmosphere to the Earth and back again into the atmosphere.

As shown in Figure 20.19, since trees absorb carbon dioxide from the air in the process of photosynthesis, forests are good examples of carbon sinks. Similarly, peatlands and wetlands are good carbon sinks. As soil is waterlogged and oxygen is limited, the dead plants in peatlands and wetlands don't fully decompose but accumulate and lock up carbon. If peatlands are dried out, the peat is exposed to air. The oxygen causes the peat to decompose and this releases carbon dioxide and methane to the air.

The carbon cycle is a natural process and, in a balanced system, the natural processes in the system recycle carbon efficiently. This helps to maintain a stable climate. However, in recent years scientists have expressed concern at the increasing levels of carbon dioxide in the atmosphere. They are worried that this may lead to what is commonly called 'global warming'. This is discussed in the next sections.

20.6 The natural greenhouse effect

You may have noticed that when a car is parked in the sun, there is an increase in temperature inside the car. The car is behaving like a garden greenhouse that traps some of the energy radiated from the Sun. The plants inside a greenhouse are kept at a higher temperature than they would be if kept outside the greenhouse.

Similarly, the Earth's atmosphere acts like a greenhouse. The Sun emits radiation which is simply energy that travels through space in the form of waves. This radiation (mainly visible and ultraviolet radiation) falls on the Earth and warms up the Earth. The Earth loses some of this heat as it cools down. However, the atmosphere helps to trap some of the energy being lost, i.e. the atmosphere helps to keep the Earth warm, Figure 20.20.

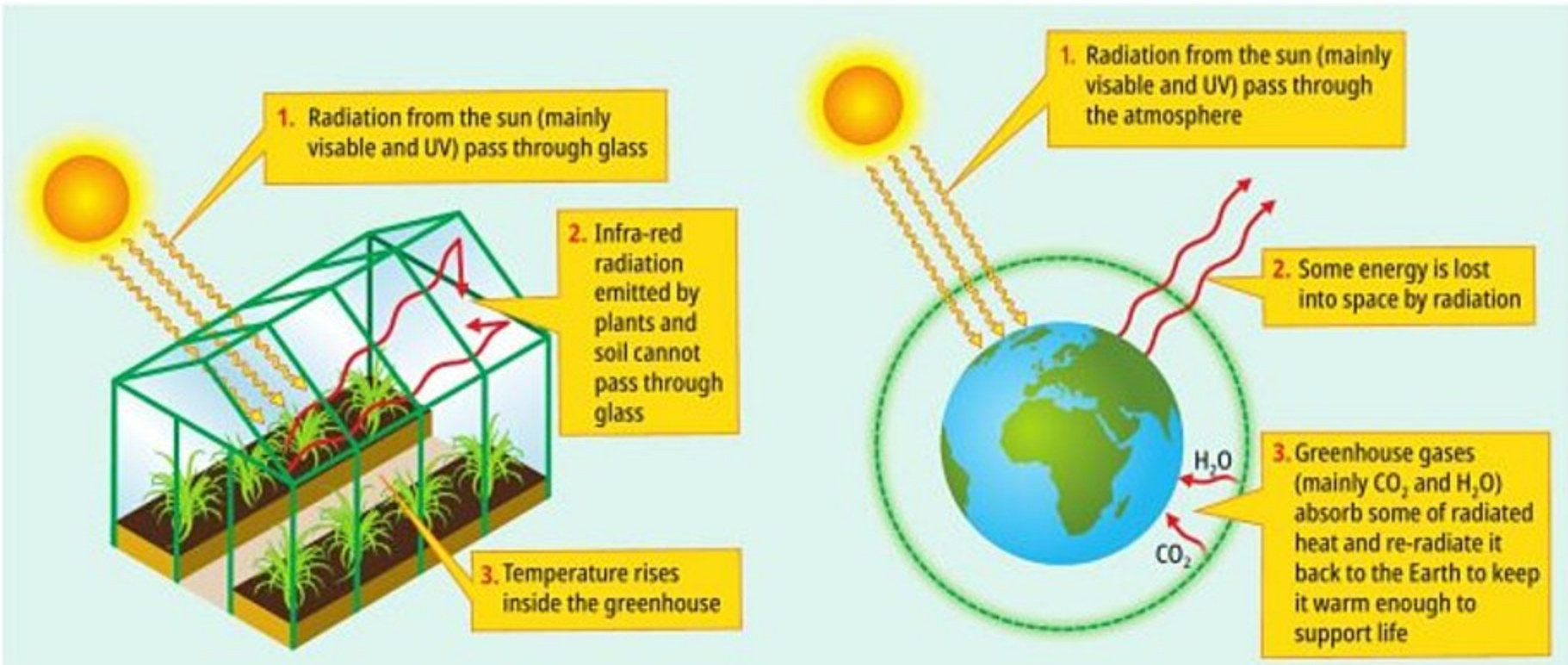

1. Radiation from the sun (mainly visable and UV) pass through glass
2. Infra-red radiation emitted by plants and soil cannot pass through glass
3. Temperature rises inside the greenhouse
1. Radiation from the sun (mainly visable and UV) pass through the atmosphere
2. Some energy is lost into space by radiation
3. Greenhouse gases (mainly CO_2 and H_2O) absorb some of radiated heat and re-radiate it back to the Earth to keep it warm enough to support life
H_2O
CO_2

Figure 20.20 The Earth's atmosphere acts like a greenhouse. It helps to trap some of the heat being lost from the Earth as it cools down.

This trapping of the Sun's energy by the atmosphere is called the **greenhouse effect**. This effect is a completely natural occurrence.

The **natural greenhouse effect** is the process by which certain gases in the Earth's atmosphere trap some of the heat energy from the Sun. This process keeps our planet warm enough to support life.

The greenhouse effect was discovered by John Tyndall, Figure 20.21.

Figure 20.21

John Tyndall
(1820–1893)

John Tyndall was born in Leighlinbridge, Carlow. He was an outstanding teacher and lectured in the Royal Institution, London where his lectures drew great crowds. He studied the ability of gases to absorb heat and found that certain gases such as water vapour absorb heat very well and keep the Earth warm. In addition to his discovery of the greenhouse effect, he also explained why the sky is blue. The Tyndall National Institute UCC is named in his honour.

The radiation from the sun consists of visible and ultraviolet radiation. This radiation enters the car and warms up items such as the seats and dashboard. These items re-radiate infra-red radiation. Infra-red radiation is an invisible radiation, but we can feel it as heat. However, the heat gets trapped inside the car because the car windows prevent the infra-red radiation passing through it. Similarly, the plants and soil inside the greenhouse do not allow the infra-red radiation to pass through the walls of the greenhouse.

Let's now take a closer look at what happens in the case of the Earth. The surface of the Earth absorbs the visible and ultraviolet radiation from the Sun and warms up. The Earth then emits infra-red radiation. This is where the chemistry starts. As you are aware, the main gases in the atmosphere are oxygen and nitrogen. However, other gases such as carbon dioxide, water vapour, methane, and oxides of nitrogen also exist in the atmosphere. These other gases absorb the infra-red radiation emitted by the Earth and re-radiate it in all directions. As shown in Figure 20.20, some of the infra-red radiation goes into space but some is sent back to the Earth's surface. This is what keeps the Earth warm enough to support life.

The natural greenhouse effect is very beneficial to us. Without this natural greenhouse effect, a lot of heat energy would be lost from the Earth into outer space. This would cause the average temperature of the air just above the surface of the Earth to fall from about 15 °C to about –15 °C (the temperature it would be if there were no atmosphere). The greenhouse effect is very important – without it the Earth would be covered by a thick sheet of ice, and life on Earth could not exist! The Moon is approximately the same distance from the Sun as the Earth. The Moon has no atmosphere surrounding it and the average surface temperature is about –18 °C.

20.7 Greenhouse gases and greenhouse factors

As discussed already, it is found that some gases in the atmosphere are particularly good at absorbing the heat energy (mainly infra-red radiation) given off as the Earth cools down. Such gases are commonly referred to as **greenhouse gases**. Carbon dioxide and water vapour are the main greenhouse gases. The other significant greenhouse gases are methane, dinitrogen oxide (nitrous oxide) and CFCs. Although the most abundant gases in the atmosphere are nitrogen (78%) and oxygen (21%), they are not greenhouse gases as they do not absorb the infra-red radiation emitted by the Earth.

Each type of greenhouse gas traps different amounts of heat. This is related to the molecular structure of each greenhouse gas and how the chemical bonds of these molecules absorb infra-red radiation. To give us a measure of how different greenhouse gases trap different amounts of heat, we use the term *the greenhouse factor*.

The **greenhouse factor** is a measure of the greenhouse effect caused by a particular gas, relative to the same amount of carbon dioxide, which is taken as the standard and is assigned a value of 1.

Thus, the greenhouse factor of a gas tells us how much heat is trapped by an individual gas in the atmosphere compared to the same amount of carbon dioxide. Since carbon dioxide is given a greenhouse factor of 1, then if a gas has a greenhouse factor of, say, 30, it means that the gas traps 30 times more heat per molecule than CO_2.

Scientists use greenhouse factors to compare how much heat a greenhouse gas traps in the atmosphere over a fixed period of time (usually 100 years) compared to carbon dioxide. To do this, they define a term called Global Warming Potential (GWP).

The global warming potentials for some greenhouse gases (over a 100-year period) are listed in Table 20.6.

The **global warming potential** of a greenhouse gas compares the amount of heat energy that one tonne of the gas would absorb compared to one tonne of carbon dioxide over the same time period (usually 100 years).

Greenhouse gas	Chemical formula	Global Warming Potential (100 years)
Carbon dioxide	CO_2	1
Methane	CH_4	30
Nitrous oxide (dinitrogen oxide)	N_2O	273
Fluorinated gases (e.g. CFCs)	Various (e.g. CFC-13 has formula $CClF_3$)	4750–14400*

Table 20.6 The main greenhouse gases and their corresponding Global Warming Potential values (*The actual value depends on the particular CFC.)

Note that carbon dioxide is the reference gas with a Global Warming Potential of 1.

Global Warming Potential is very useful because it takes into account not only how strongly the gas traps heat, but also how long the gas stays in the atmosphere.

Different greenhouse gases have different impacts on the greenhouse effect because:

1. Different gases have different abilities to absorb heat (infra-red) energy, i.e. they have different greenhouse factors and different Global Warming Potential values.
2. Different gases are present in different quantities (abundances), Table 20.7.
3. Different gases have different residence times in the atmosphere, i.e. they are broken down at different rates.

Greenhouse gas	Abundances (approximate)	Residence times
Carbon dioxide	420 ppm	100–1000 years
Methane	1.9 ppm	12 years
Nitrous oxide (dinitrogen oxide)	0.33 ppm	114 years
Fluorinated gases	0.00001 ppm	Up to thousands of years

Table 20.7 The main greenhouse gases, their abundances in the atmosphere and their residence times.

Since water vapour is the most abundant greenhouse gas, it has a greater greenhouse effect than carbon dioxide. Let's now have a closer look at water as a greenhouse gas.

Water vapour as a greenhouse gas

Water vapour is a very powerful greenhouse gas, as it traps heat in the atmosphere and keeps the Earth warm – just like carbon dioxide, methane and other gases. In fact, it is estimated that water vapour is responsible for about 50–60% of the Earth's natural greenhouse effect. If you look at Table 20.6 you will see that water vapour is not included or assigned a GWP factor. The reason for this is that, to be assigned a GWP, a gas must satisfy certain criteria:

(i) We release a set number of kg of it

(ii) It stays in the atmosphere for a known time

(iii) It directly causes warming on its own.

- However, humans do not directly control the amount of water vapour in the atmosphere. Water vapour responds to changes in temperature and increases warming that is already happening. In other words, greenhouse gases such as CO_2, CH_4 and N_2O when released by human activity start the warming process. However, water vapour just increases the warming but does not directly cause the heat increase. Increasing the concentrations of CO_2, CH_4 and N_2O is like turning on a heater in a room, as they cause the temperature of the atmosphere to increase. Water vapour is like the insulation in the walls of the room that keeps the heat in the room. It keeps the room warmer but only after the heater is turned on, Figure 20.22.

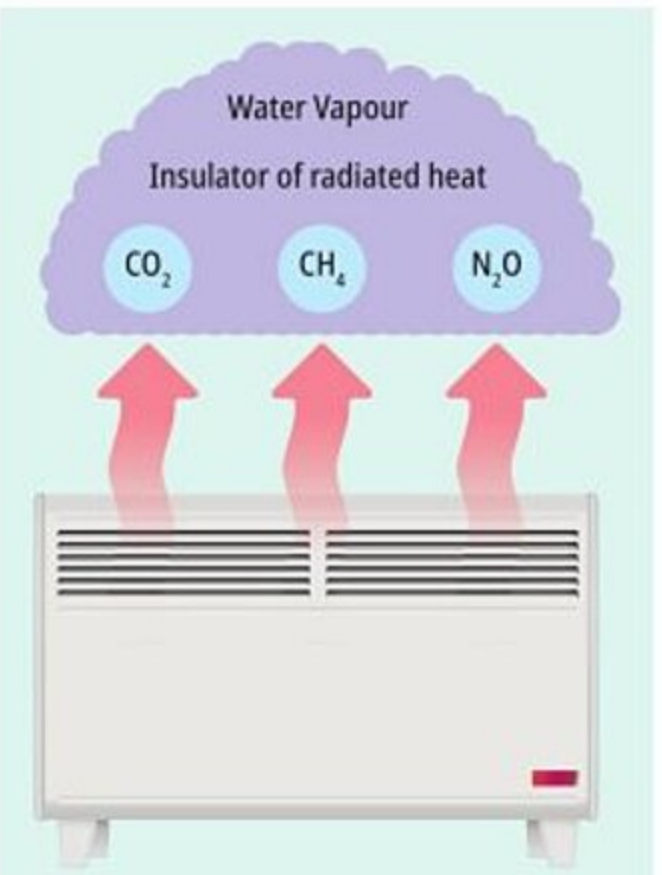


Figure 20.22 Water vapour increases warming by helping to trap the heat, but does not directly cause the heat increase.

- Most water vapour comes from natural evaporation from sources such as oceans, lakes and plants. As the Earth gets warmer (due to CO_2, CH_4 and N_2O), more water vapour evaporates, and the warmer air holds more water vapour. We don't emit water vapour directly into the atmosphere in a way that affects our climate in the long term. In other words, the concentration of water in the atmosphere depends on temperature, not direct emissions. Therefore, it would not make sense to assign it a GWP value in the same way that we assign to gases that we add directly to the atmosphere.
- Water vapour stays in the atmosphere for just a few days or weeks before condensation takes place and it falls as rain. This is in contrast to gases such as CO_2, CH_4 and N_2O, which can stay in the atmosphere for many years. The short lifetime of water means that it is not possible to compare water vapour to other gases over a 100-year period, as required in calculating GWP values.

20.8 The enhanced greenhouse effect

It is of great concern to everybody that increasing concentrations of greenhouse gases in the atmosphere are causing the Earth to get warmer. This occurrence is called the **enhanced greenhouse effect**.

In other words, the enhanced greenhouse effect takes place when extra greenhouse gases increase the amount of heat trapped in the Earth's atmosphere above the natural level.

The extra warming that results from the enhanced greenhouse effect is called **global warming**.

Evidence for the enhanced greenhouse effect may be summarised as follows:

The **enhanced greenhouse effect** is an intensification of the Earth's natural greenhouse effect due to increased concentrations of greenhouse gases in the atmosphere caused by human activities, such as burning fossil fuels and deforestation

1. Rising carbon dioxide levels

The concentration of carbon dioxide in the atmosphere plotted against time since 1958 is shown in Figure 20.23.

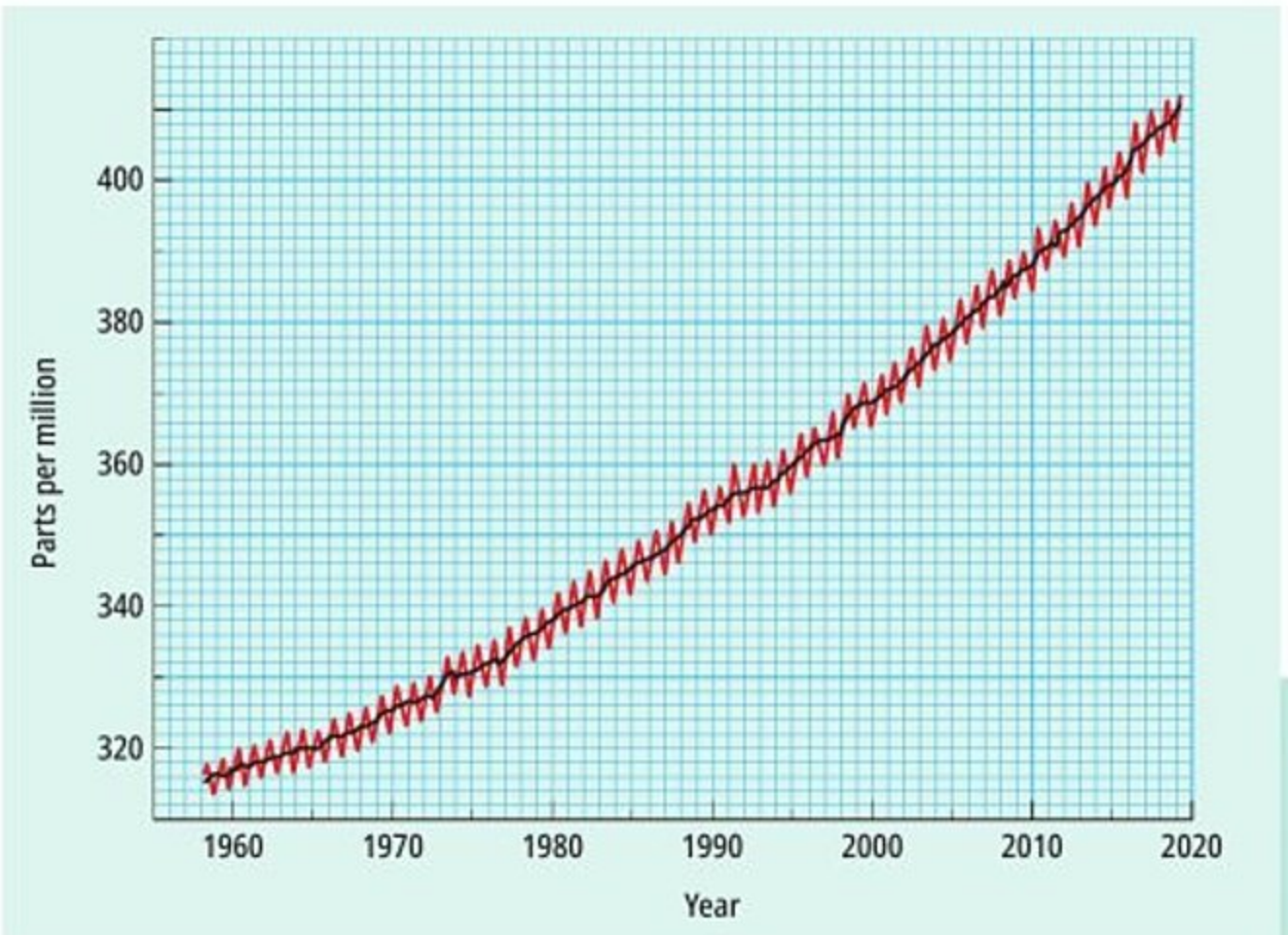


Figure 20.23 Accurate measurements of the concentration of carbon dioxide in the atmosphere have been made in Hawaii since 1958. The rising levels are giving cause for concern.

The levels of carbon dioxide in the Earth's atmosphere are rising as a result of more fossil fuels being burned due to increasing industrialisation. The rise in levels of carbon dioxide became particularly obvious in the 1970s and has caused considerable debate about the effect of the carbon dioxide increase on the Earth's climate. Over the past 100 years, the amount of fossil fuels being burned has increased by about 4% each year. It has been estimated that the burning of fossil fuels in Ireland produces an average of about 16,000 tonnes of carbon dioxide per year.

In Figure 20.23, note that within any one year the levels rise and fall. This is because, as plants grow in the spring and summer, photosynthesis uses up carbon dioxide, causing the level in the atmosphere to fall. In the winter and autumn, the level of carbon dioxide rises again as less photosynthesis is occurring as plants decay.

The contribution of greenhouse gases to global warming is shown in Figure 20.24.

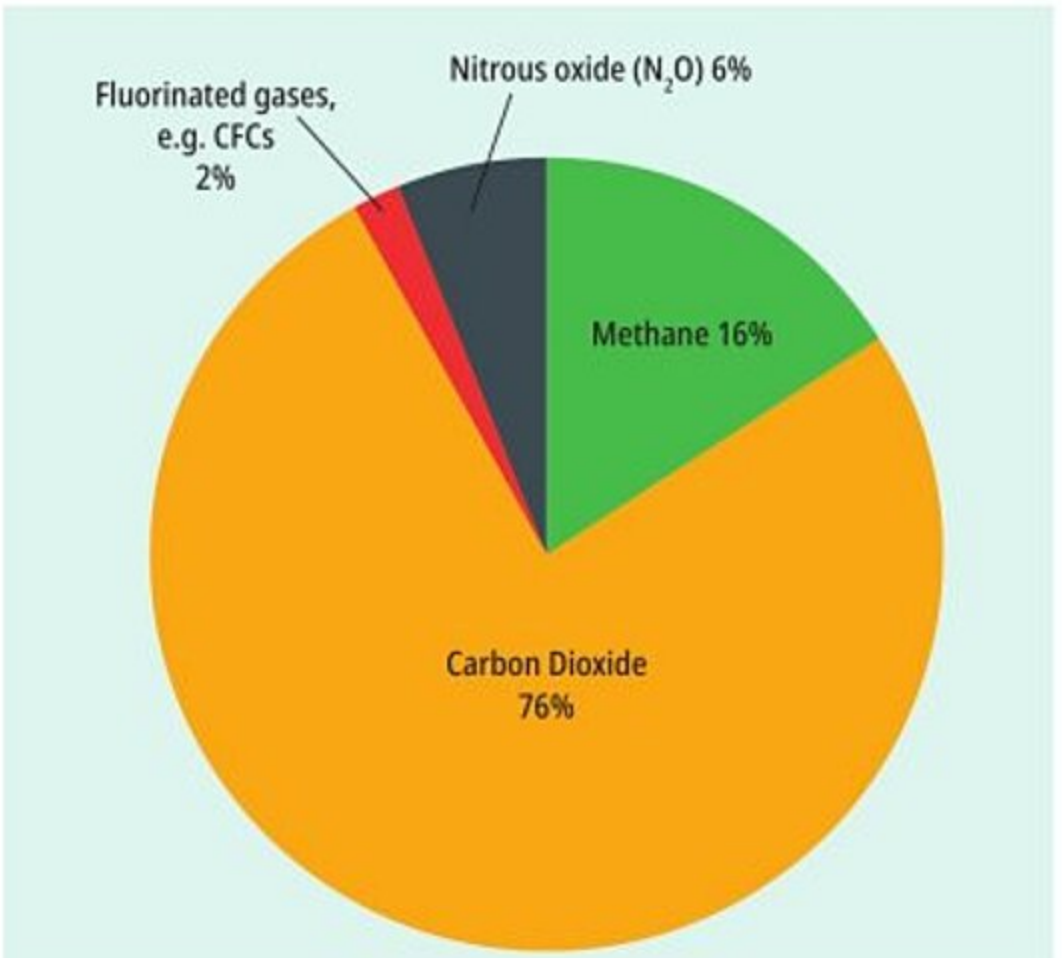


Figure 20.24 The main greenhouse gases (other than water vapour) and the approximate contribution they make to the greenhouse effect

2. Global temperature rise

Since 1880 the average surface temperature of the Earth has risen by over 1.1 °C. Most of this increase has occurred since 1970. The speed of global temperature rise cannot be explained by natural factors alone. However, it can be explained when human influences on emissions of greenhouse gases are taken into consideration.

3. Matching of climate computer models

Computer models are used to study the Earth's climate. When only natural factors are included, the models do not match the observed warming. However, when human emissions are included, the models accurately match the temperature rise. This is very strong evidence that human activity is responsible for the enhanced greenhouse effect.

Water vapour is also a greenhouse gas and has a greater overall effect than carbon dioxide due to its higher concentration. (You may have noticed that, if there are no clouds in the sky, the nights can be very chilly. This is because heat is rapidly escaping from the Earth as there is little water vapour to redirect the escaping infrared radiation back to the Earth.) However, the global concentration of water vapour is not affected to any great extent by human activities. The amount of water vapour in the atmosphere depends on temperature and is controlled by evaporation and condensation in the water cycle.

On the other hand, it is found that the rate of 'turnover' of carbon dioxide in the atmosphere is quite slow. As already mentioned, this 'turnover' rate of carbon dioxide is referred to as the **residence time** for carbon dioxide. Although the sea can dissolve a lot of carbon dioxide, the top few hundred metres of sea water mix very slowly with deeper waters. This means that, when carbon dioxide dissolves in seawater, it can take hundreds of years before it penetrates deep down in the ocean and is precipitated as calcium carbonate. Thus, although the oceans will eventually dissolve much of the increased levels of carbon dioxide in the atmosphere, this will take a long time. It is estimated that carbon dioxide has a residence time of about 100 years, i.e. the average molecule of carbon dioxide remains in the atmosphere for about 100 years. Photosynthesis is the process that removes carbon dioxide from the atmosphere at the greatest rate. However, this cannot keep pace with the rate at which carbon dioxide is being released into the atmosphere by burning fossil fuels.

The concentration of other greenhouse gases in the atmosphere are also affected by human activity, e.g. methane (from natural gas leakage, landfill rubbish dumps, swamps, paddy fields and ruminants), dinitrogen oxide (use of nitrogenous fertilisers) and CFCs (from old fridges, foams and aerosol sprays). Although there are only very small amounts of CFCs in the atmosphere, each molecule has a big effect, since CFCs have a large greenhouse factor. Therefore, it is important that steps are taken to limit the amounts of these substances released into the atmosphere.

Consequences of the enhanced greenhouse effect

The consequences of the enhanced greenhouse effect are illustrated in Figure 20.25 and may be summarised as follows:

1. **Global warming.** The Earth's average surface temperature is rising and most of this increase has occurred since the 1970s. Since water expands as the temperature increases, it is expected that sea levels will rise. It is also expected that sea levels could be affected by the melting of glaciers in the Arctic and Antarctic regions. Global sea levels have risen by about 20 cm since 1900. This could be quite serious and could adversely affect the homes and livelihoods of people in low-lying countries such as the Netherlands and Bangladesh.

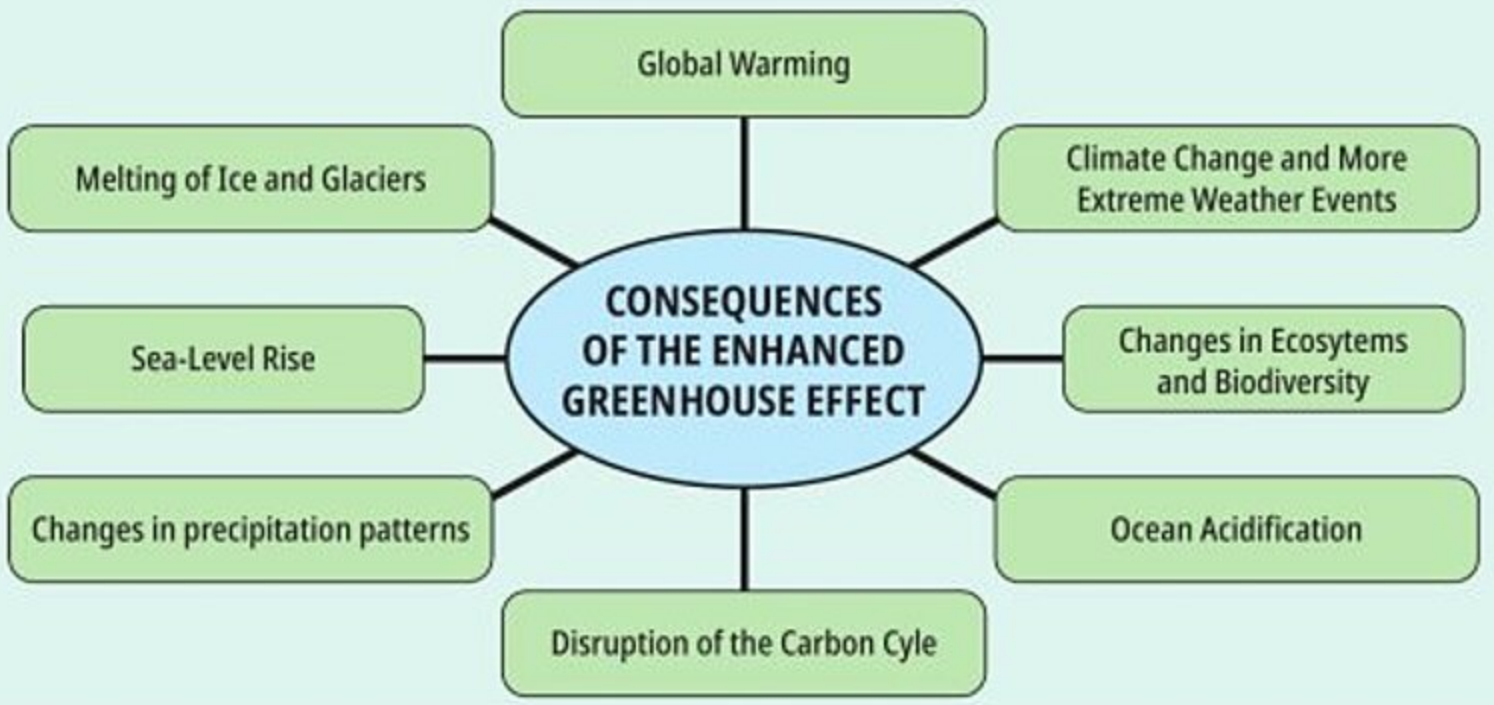

Global Warming
Melting of Ice and Glaciers
Climate Change and More Extreme Weather Events
CONSEQUENCES OF THE ENHANCED GREENHOUSE EFFECT
Sea-Level Rise
Changes in Ecosytems and Biodiversity
Changes in precipitation patterns
Ocean Acidification
Disruption of the Carbon Cyle

Figure 20.25 Some consequences of the enhanced greenhouse effect

2. **Climate changes and more extreme weather events.** It is expected that, as the temperature of the atmosphere is increased, more violent weather disturbances will be observed – storms will be more frequent and more violent. This is because more energy will be contained in the air and water vapour at the Earth's surface. Climate conditions in general will become more extreme, and data from climate conditions in the past will be less reliable.

3. **Changes in precipitation (rain, snow, hail) patterns.** As the temperature of the atmosphere is increased, the warmer air will increase evaporation of water. Since water vapour is itself a greenhouse gas, increased levels of water vapour will result in increased warming. Warmer air can hold more moisture and, therefore, heavier rain can fall. Therefore, some regions of the world will experience more intense rainfall and flooding will result.

   However, in some subtropical regions, rising temperatures increase evaporation from soil, which increases the occurrence of droughts. More prolonged droughts are now being experienced in many regions

4. **Ocean acidification.** This term refers to the ongoing decrease in the pH of the Earth's oceans caused by the dissolving of carbon dioxide from the atmosphere in water. Carbon dioxide dissolves in water to form carbonic acid:

$$CO_2 + H_2O \rightarrow H_2CO_3$$

   As greater quantities of carbon dioxide dissolve in the oceans, this makes it more difficult for marine organisms to survive. For example, the shells or exoskeletons of many marine organisms such as oysters, clams and mussels are built from calcium carbonate. Carbonic acid reacts with calcium carbonate to give off carbon dioxide. Thus, the organisms die as the solid shell or exoskeleton is destroyed.

$$\underset{\text{solid}}{CaCO_3} + H_2CO_3 \rightarrow \underset{\text{soluble}}{Ca^{2+} + 2HCO_3^-}$$

5. **Ecosystems and biodiversity.** The rising temperature of the Earth and the change in weather patterns can disrupt the balance in many natural ecosystems. Some animals may be forced to migrate to cooler areas and those that cannot move or adapt quickly enough may decline in population or become extinct. Climate change may cause droughts and floods which destroy habitats, e.g. ice melting in polar regions. These changes can impact on food supply, e.g. fewer pollinators result in fewer crops. Also, the decline in the marine population can result in lower availability of fish.

Other greenhouse gases

So far, we have studied the main greenhouse gases. There are two other categories of greenhouse gases listed on the syllabus that we are studying. We will now briefly discuss these.

NOx greenhouse gases

The term 'NOx gases' refers to two gases called nitrogen monoxide (NO) and nitrogen dioxide (NO_2). (The old name for nitrogen monoxide was nitric oxide.) These gases are emitted when fossil fuels such as petrol and diesel are burned at high temperature in car engines, Figure 20.26. Do not confuse these gases with the gas N_2O (nitrous oxide or dinitrogen oxide) which contributes to the greenhouse effect as a result of nitrogenous fertilisers.

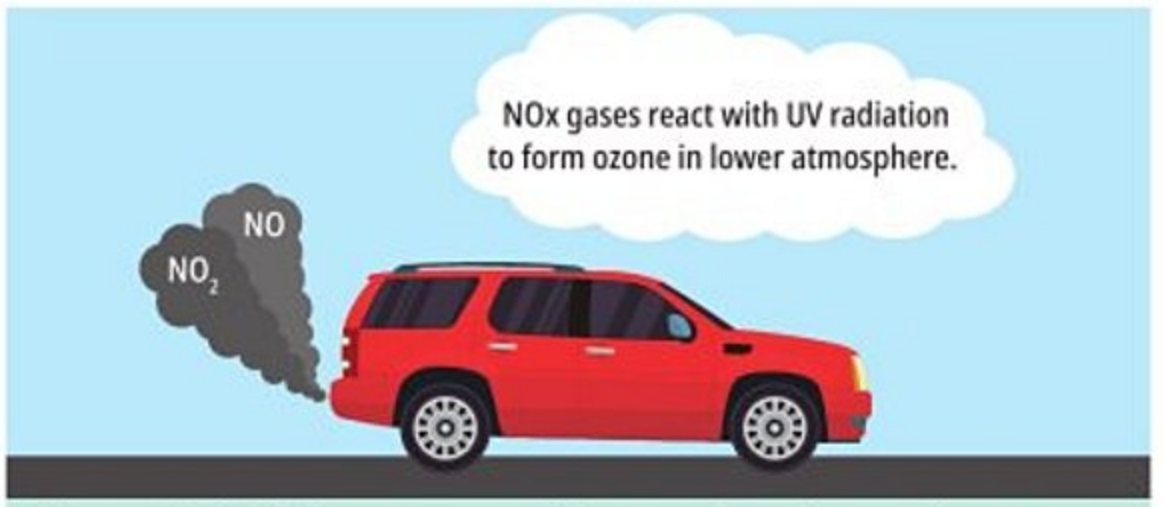


Figure 20.26 NOx gases contribute to the enhanced greenhouse effect both directly and indirectly due to the formation of ozone near the surface of the Earth.

The impact of NOx on the enhanced greenhouse effect is a bit complicated but the following are the key points:

- Nitrogen monoxide is not considered a greenhouse gas by itself. However, on emission from car engines, it reacts with the air to form nitrogen dioxide.

$$2NO + O_2 \rightarrow 2NO_2$$

- Nitrogen dioxide does contribute to the enhanced greenhouse effect but only very weakly compared to the other greenhouse gases.

In addition to this direct effect on the enhanced greenhouse effect, the NOx gases also indirectly contribute to the greenhouse effect because they help form ozone in the lower atmosphere. (You may have heard of ozone because of its importance in the upper atmosphere in protecting us from harmful UV radiation.) The ozone in the lower atmosphere acts as a greenhouse gas which helps to trap heat near the Earth's surface.

Sulfur oxides

Sulfur dioxide (SO_2) and sulfur trioxide (SO_3) do not significantly contribute to the greenhouse effect. They are not direct greenhouse gases as they do not trap heat directly. The gases are produced by burning fossil fuels containing sulfur and also in volcanic eruptions.

These gases react in the atmosphere to form aerosols – tiny droplets of sulfuric acid suspended in air. These aerosols reflect sunlight back into space, causing a cooling effect.

20.9 The significance of the carbon cycle in relation to natural and human-influenced climate change and sustainability

The above topic is listed on the Leaving Certificate chemistry curriculum. You could be asked an essay-style question on this topic, similar to that given on the SEC sample exam paper. Therefore, in your essay, it is important to cover some key points. The mind map shown in Figure 20.27 may be of assistance to you or you may prefer to draw your own mind map.

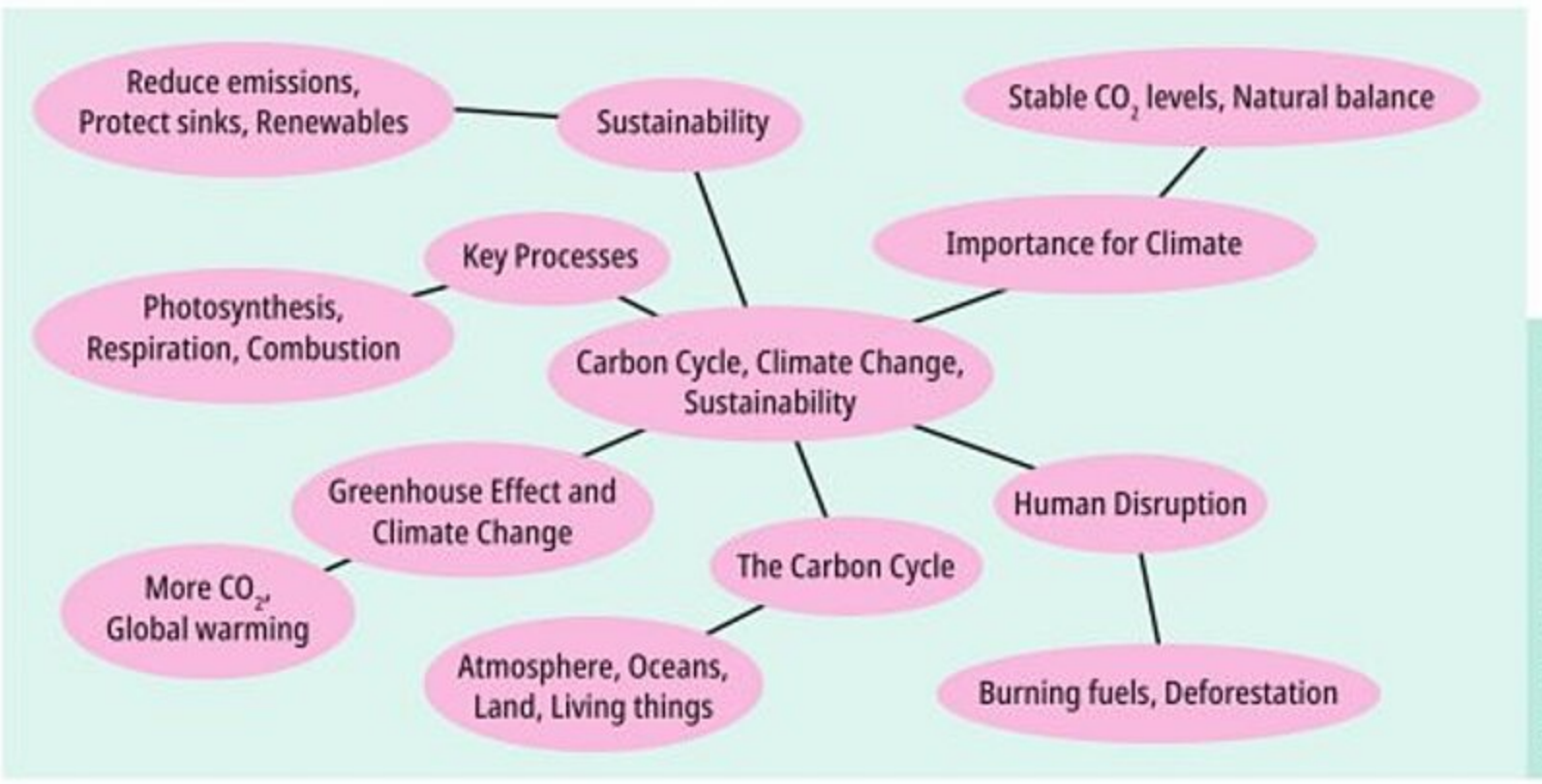


Figure 20.27 Mind map summarising some key points about the significance of the carbon cycle in relation to natural and human-influenced climate change and sustainability

- Outline what the carbon cycle is all about and refer to carbon in the atmosphere, oceans, land and living things.
- Refer to key processes such as photosynthesis, respiration, combustion, decomposition and the dissolving of carbon dioxide in oceans and waterways.
- Discuss why the carbon cycle is important for climate and how, under natural conditions, a balanced system exists that keeps the concentration of CO_2 at a stable level.
- Explain what happens when the carbon cycle is disrupted by human influences (e.g. burning fossil fuels and cutting down forests) that add more carbon to the cycle than the natural systems (natural carbon sinks) can handle.
- Explain that trees are natural carbon sinks. When they are cut down, less CO_2 is absorbed due to loss of photosynthesis and the burning or decay of the tree releases the stored carbon as CO_2.
- Explain that more CO_2 in the atmosphere results in a more intense greenhouse effect and that this gives rise to global warming and climate change.
- State that sustainability is the use of a resource so that it does not run out.
- Explain that to live sustainably we need to understand the carbon cycle and ensure that it is kept in balance.
- Outline that sustainability involves reducing carbon emissions, e.g. move away from burning fossil fuels to generate electricity and switch to renewable energy. Also we need to protect carbon sinks such as oceans and forests and to plant trees to offset emissions.
- Outline some consequences of the enhanced greenhouse effect – rise in sea levels, climate change, effect on agriculture.

20.10 Solutions to anthropogenic influences on the atmosphere

The word 'anthropogenic' comes from the Greek words *anthropos*, meaning 'human being' and *gen-* meaning 'be produced'. In the English language, it means 'resulting from human activity'. Thus, we now study the possible solutions to the changes in the composition of the atmosphere that are caused by human actions.

The main anthropogenic influences on the atmosphere and possible solutions to the impacts of these influences are summarised in Table 20.7. You are advised to study Table 20.7 carefully as the topic of *possible solutions to anthropogenic influences on the atmosphere* is specifically mentioned on the syllabus that we are studying.

Human activity	Influence on atmosphere	Possible solutions
1. Burning fossil fuels	This releases greenhouse gases (mainly CO_2, CH_4 and N_2O).	• Switch to renewable energy sources such as solar, wind and hydroelectricity. • Improve energy efficiency in buildings (better insulation), industry (recycling of energy) and transport (greater fuel efficiency) • Phase out fossil fuels such as coal, natural gas and oil.
2. Deforestation and draining of peatlands and wetlands	There are fewer trees and peatlands are drained. This results in less carbon dioxide being taken out of the atmosphere.	• Create more carbon sinks by planting more trees. • Protect peatlands and wetlands as these are good carbon sinks.
3. Transportation	Transportation using fossil fuels emits greenhouse gases (e.g. CO_2 and N_2O).	• Use sustainable transport (e.g. cycling, walking and public transport). • Use biofuels to achieve lower carbon footprint.
4. Agriculture	Agricultural activity produces CH_4 from livestock and N_2O from fertilisers.	• Reduce methane production inside animals with the aid of special feeds. • Breed animals that naturally produce less methane. • Install biogas systems to collect methane from animal manure and food waste. Biogas can be used to fuel vehicles or inject into natural gas pipelines. • Use fertilisers more efficiently (correct amount at the correct time) and plant nitrogen-fixing crops to reduce the need for artificial fertilisers.
5. Industrial processes	Industrial activity produces CO_2 from burning fossil fuels for energy and chemical reactions. Cement production is a major emitter of CO_2. N_2O is emitted in the manufacture of nitric acid and nylon.	• Switch from fossil fuels to renewable energy sources. • Improve energy efficiencies in industrial plants, e.g. better insulation, more efficient motors and more efficient production methods. • Install a carbon capture system.
6. Waste and landfills	CH_4 is released when organic matter is broken down by bacteria in the absence of oxygen (anaerobic respiration or fermentation).	• Install pipes in landfills to collect methane. The biogas can be burned to generate electricity instead of allowing it to escape into the atmosphere. CO_2 formed has lower GWP than CH_4. • Reduce food waste. • Recycle carbon-based materials such as paper and wood.

Table 20.8 Summary of some possible solutions to anthropogenic influences on the atmosphere

The term **carbon capture** (mentioned in point 5 in Table 20.8) is also called **carbon capture and storage**. This is a process where carbon dioxide is trapped before it enters the atmosphere and then stored safely (often underground).

Carbon capture is a way of trapping carbon dioxide gas before it goes into the atmosphere, and storing it so that it cannot contribute to global warming.

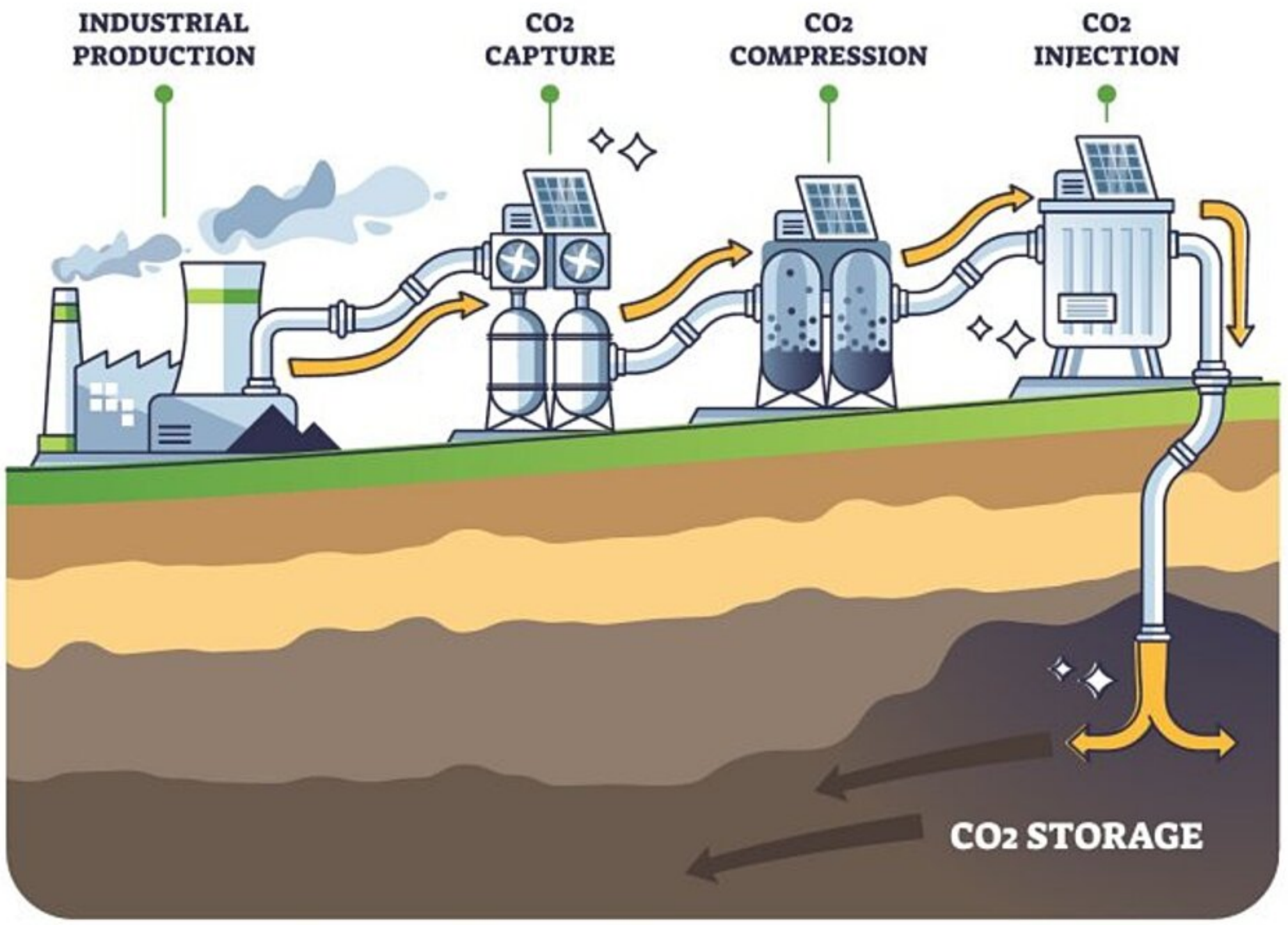


Figure 20.28 Some industries install carbon capture systems which trap carbon dioxide before it goes into the atmosphere.

Carbon capture is used in power plants and factories that produce carbon dioxide (usually by burning fossil fuels), Figure 20.28. The carbon dioxide is removed from chimneys after burning has taken place. It is compressed into a liquid and transported via pipelines or trucks. It is then pumped into oil or gas fields that are no longer in use.

Recall that methane is a very powerful greenhouse gas and traps about 30 times more heat than carbon dioxide. Therefore, even if methane is burned to form carbon dioxide and water, the global warming effect is lessened.

Note that many of the suggested solutions in Table 20.8 involve us as individuals contributing to sustainability. You may recall in your study of Junior Cycle Science meeting the idea of carbon footprint.

A carbon footprint tells us how much we are adding to climate change by the way we travel, shop, recycle and other activities in our everyday lives.

TEST YOURSELF: Attempt Questions 20.6–20.7 and W20.7–W20.19.

Carbon footprint is a measure of the amount of carbon dioxide released into the atmosphere as a result of the activities of a particular individual, organisation or community through burning fossil fuels.

Summary What I should know

- Water contamination is the introduction of substances into water that make it unsafe for consumption or harmful to ecosystems.
- Biochemical oxygen demand (B.O.D.) is defined as the amount of dissolved oxygen consumed by biological (biochemical) action, when a sample of water is kept at 20 °C, in the dark, for five days.
- Eutrophication is the enrichment of water with nutrients, leading to excessive growth of algae and other plants.
- Flocculation is the coming together (coagulating) of small, suspended particles in water into larger particles.
- Treatment of drinking water involves screening, flocculation, sedimentation, filtration, chlorination, pH adjustment and UV treatment.
- Water treatment has energy and environmental impacts.
- The carbon cycle describes the process in which carbon continuously travels from the atmosphere to the Earth and back again into the atmosphere.
- The natural greenhouse effect is the process by which certain gases in the Earth's atmosphere trap some of the heat energy from the Sun. This process keeps our planet warm enough to support life.
- The enhanced greenhouse effect is an intensification of the Earth's natural greenhouse effect due to increased concentrations of greenhouse gases in the atmosphere caused by human activities, such as burning fossil fuels and deforestation.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain various causes of water contamination and the biochemical consequences.			
Identify the problems caused by microplastics in our environment.			
Describe and discuss what happens in each stage of water treatment.			
Evaluate the role of the carbon cycle in both the natural greenhouse effect and the enhanced greenhouse effect.			
Summarise the evidence for the enhanced greenhouse effect and discuss its consequences.			
Outline solutions to anthropogenic influences on the atmosphere.			

Chapter review questions

20.1 **(a)** The decomposition of sewage reduces the amount of a certain gas dissolved in water. Name the gas.

(b) Name one pollutant that may be contained in industrial effluent.

(c) The runoff of nitrates and phosphates from farms into rivers can cause an overgrowth of algae. What name is used to describe this overgrowth of algae?

(d) What term is used to describe tiny plastic particles less than 5 mm in size?

20.2 **(a)** What happens to the solubility of oxygen in water as temperature increases?

(b) When organic waste is discharged into water, bacteria break it down. What gas is used up in this process?

(c) If oxygen levels fall too low, certain bacteria take over and produce hydrogen sulfide (H_2S). What name is given to this type of bacteria?

(d) What noticeable effect does H_2S gas have on water?

20.3 **(a)** What is meant by the term *eutrophication*?

(b) Eutrophication can occur naturally. Describe another way that eutrophication can occur.

(c) High levels of certain ions lead to rapid plant and algal growth. Name two of these ions.

(d) Rapid algal growth can lead to a green scum on the water surface. What name is given to this green scum?

(e) What health problems are thought to be caused by high levels of nitrate ions in water?

20.4 **(a)** Drinking water should be colourless, odourless and safe to drink. Name one other property of drinking water that is required by law.

(b) What name is given to the water taken from rivers and lakes before it is treated?

(c) In the treatment of drinking water, what process removes large floating debris like twigs and leaves?

(d) Name the process that causes suspended solids to clump together into larger particles.

20.5 **(a)** For what purpose is energy used in the flocculation process?

(b) Name two diseases that are prevented by having safe drinking water.

(c) Explain how plastic waste is prevented by drinking tap water.

(d) Outline one negative impact of water treatment in terms of disposal of waste.

(e) The use of treatment chemicals in treatment of water can impact on the production of carbon dioxide emissions. Explain how this could occur.

20.6 The levels of carbon dioxide in the atmosphere are increasing.

(a) Give two reasons why this is happening.

(b) Explain how the atmosphere around the Earth acts like the glass in a greenhouse.

(c) What is meant by the *enhanced greenhouse effect*?

(d) Why is the enhanced greenhouse effect causing concern to scientists?

(e) Name any two greenhouse gases that do not contain carbon.

(f) Suggest two steps that could be taken to stop the increase in the levels of greenhouse gases in the atmosphere.

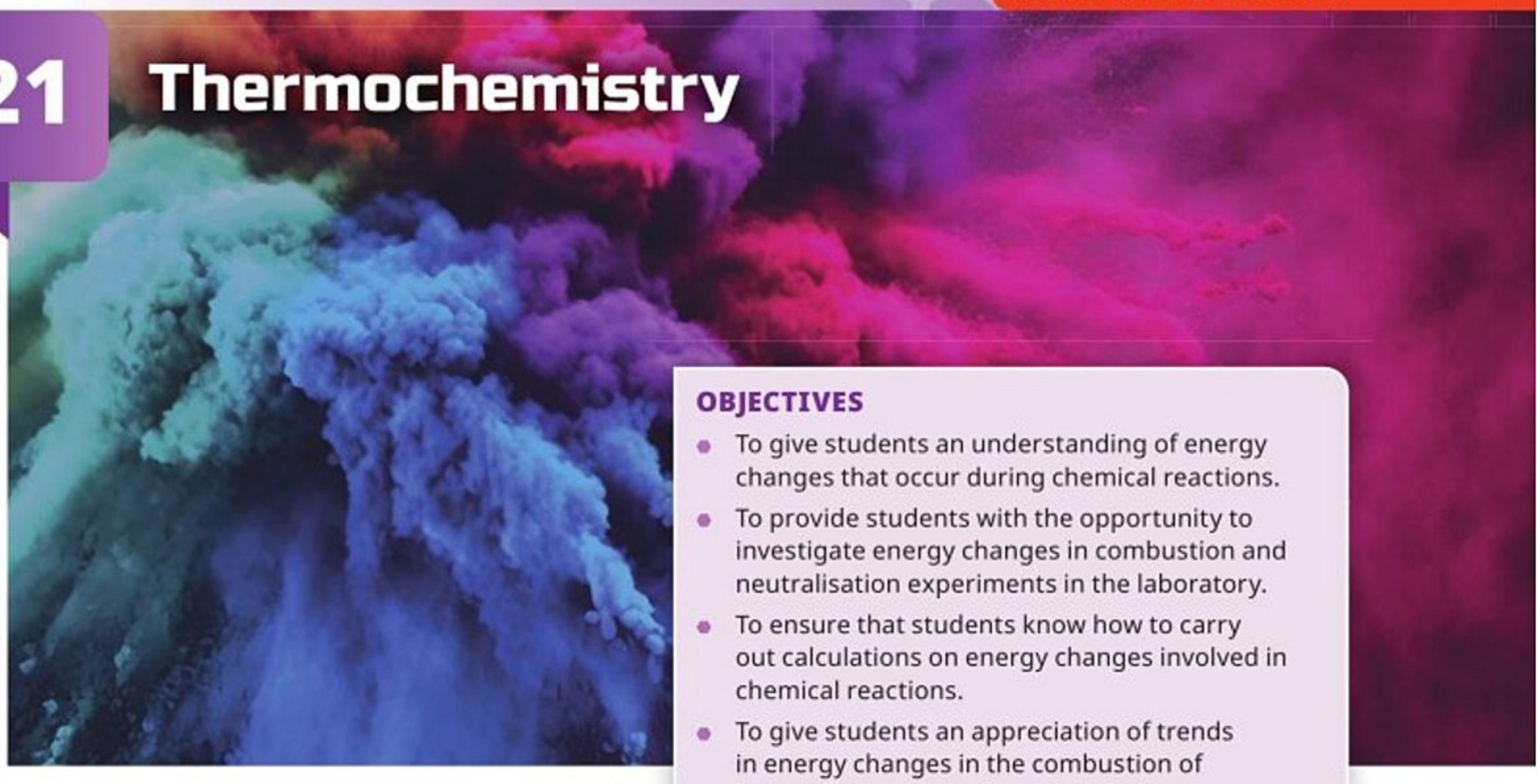
20.7 **(a)** 'The greenhouse effect is of great benefit and the Earth would be a very different place without it.' Discuss this statement.

(b) Explain the term *Global Warming Potential* and arrange any three greenhouse gases in increasing order of their Global Warming Potential values.

(c) Explain why water is not assigned a Global Warming Potential value.

(d) Why do tropical forests and jungles play such a large part in ensuring a balance between the levels of carbon dioxide and oxygen in the atmosphere?

21 Thermochemistry



OBJECTIVES

- To give students an understanding of energy changes that occur during chemical reactions.
- To provide students with the opportunity to investigate energy changes in combustion and neutralisation experiments in the laboratory.
- To ensure that students know how to carry out calculations on energy changes involved in chemical reactions.
- To give students an appreciation of trends in energy changes in the combustion of hydrocarbons and primary alcohols.

21.1 Introduction

The transfer of energy between chemical substances plays an important part in our lives. For example, the burning of fuels in air releases large amounts of energy to provide us with heat for our homes or fuel for transport. The reaction of glucose and oxygen during respiration in the cells of our bodies releases energy to keep us active and alive. Photosynthesis occurs when plants absorb energy from sunlight to enable carbon dioxide and water molecules to react together to form glucose molecules. The branch of chemistry which studies the heat changes that occur during chemical reactions is called **thermochemistry**.

Thermochemistry is the study of heat changes that occur during chemical reactions.

Thermochemistry is also called **chemical thermodynamics** from the study of engines and the relationship between heat and movement. We will find that the study of thermochemistry will be a great help to us in areas such as predicting whether a reaction gives off heat or takes in heat, Figure 21.1, or comparing fuels to decide which are the most efficient ones to use.

Enthalpy (*H*) is the total heat content that is stored in a chemical system.

21.2 Enthalpy and enthalpy change

The word 'enthalpy' is used to describe the total heat content of a chemical system (both reactants and products). The symbol for enthalpy is *H* (H for heat) and it is measured in kilojoules (kJ).

Whenever we use the term *chemical system* we are referring to the reactants and products. When we speak about heat being lost to the 'surroundings', we mean what is outside the chemical system. For example, if we mix two chemicals in a beaker and heat is generated, it is often said that this heat is 'lost to the surroundings', e.g. to the air in the laboratory.

Figure 21.1 This instant cold-pack works by mixing together two chemicals inside the packet. The temperature falls when these two chemicals react together.

It is impossible to directly measure the enthalpy of reactants or products. The reason for this is because enthalpy refers to the total energy stored in a substance. This total energy is rather complicated, as energy is stored in chemical bonds, energy is stored as kinetic energy in moving particles, energy is stored as particles vibrate, and energy is also related to how particles collide against the sides of containers.

So instead of trying to measure enthalpy itself, we focus on what we **can** measure. We can easily measure the enthalpy **changes** that take place during a chemical or physical process. The symbol for enthalpy change is ΔH and it is measured in kilojoules (kJ). The symbol Δ is pronounced 'delta' and is often used in mathematics to indicate change.

Enthalpy change (ΔH) is the overall energy exchanged with the surroundings when a chemical reaction or physical change is carried out at constant pressure.

You may wonder why the definition includes reference to 'constant pressure'. In most experiments, the pressure of the system does not change. For example, chemical reactions carried out in open containers such as beakers and conical flasks take place at atmospheric pressure. If an experiment is being carried out in a closed container, then some energy might be lost in changing the volume of the system, e.g. pushing against the plunger of a syringe. In short, by carrying out experiments under constant pressure, we ensure that any energy changes are due only to loss or gain of heat energy.

Thermochemical equations

Chemists use the symbol ΔH ('delta H') to indicate the heat change taking place when a chemical reaction occurs. For example, hydrogen is a fuel that burns in oxygen to form water. We can write a balanced equation as follows:

$$H_{2(g)} + \tfrac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H = -242 \text{ kJ mol}^{-1}$$

- Equations such as the above are called **thermochemical equations**.
- This equation tells us that when one mole of hydrogen reacts with half a mole of oxygen to form one mole of steam, 242 kilojoules of heat are released.

By convention, **a negative value of ΔH indicates an exothermic reaction**. Any chemical reaction that produces heat is called an exothermic reaction. ('Ex' is the Latin word for 'out of'.)

- A positive value of ΔH indicates an endothermic reaction.
- The kJ stands for kilojoules. The SI unit of energy is the joule (J). Since one joule of heat energy is rather small, heat changes when molar quantities react are normally measured in kilojoules (1 kJ = 1000 J).
- The mol^{-1} in the above equation indicates that we are working in moles rather than molecules, i.e. the heat measured refers to 1 **mole** of H_2 reacting with half a **mole** of O_2 to form 1 **mole** of water H_2O.
- The ΔH value above is commonly referred to as the **enthalpy of reaction** and is defined as follows.

Enthalpy of reaction (ΔH) is the heat change when the numbers of moles of reactants indicated in the balanced equation for the reaction react completely at constant pressure.

If the numbers of moles in the balanced equation are changed, then the enthalpy of reaction also changes. For example, if we burn twice the number of moles of hydrogen, the enthalpy of reaction is doubled:

$$2H_{2\,(g)} + O_{2\,(g)} \rightarrow 2H_2O_{(g)} \qquad \Delta H = -484 \text{ kJ mol}^{-1}$$

Note: The physical states of the reactants and products (solid, liquid or gas) are always given in thermochemical equation. Sometimes you may also see *(aq)* to indicate that the substance is dissolved in water. States of reactants and products are included because changing the physical states of either reactants or products can alter the value of ΔH.

Thermochemical equations must be balanced, the value of ΔH must be written in and the physical states of reactants and products must be given. In books of data containing these thermochemical equations, the temperature at which the given enthalpy of reaction is measured is always stated. This is usually 25 °C.

Exothermic reactions

Enthalpy changes can be illustrated on Enthalpy Profile Diagrams, Figure 21.2. Note that Enthalpy Profile Diagrams are similar to the Reaction Profile Diagrams that we met in Chapter 17 except that, instead of emphasising activation energy, we are now emphasising enthalpy changes. In Figure 21.2, the enthalpy of the reactants is greater than that of the products. Therefore, heat is given out when the reaction takes place.

Some examples of exothermic reactions are:

(i) Combustion. The term *combustion* is used to describe a chemical reaction in which a substance reacts with oxygen to produce heat (and often light). *Combustion* is the scientific term for the everyday word 'burning'. The term *combustion* explains the chemistry of what happens when burning takes place.

One of the most important properties of fuels is that they burn in air. The burning of fuels always produces heat. An example of a combustion reaction is the burning of methane (found in natural gas), Figure 21.3.

$$\underset{\text{methane}}{CH_{4(g)}} + \underset{\text{oxygen}}{2O_{2(g)}} \rightarrow \underset{\text{carbon dioxide}}{CO_{2(g)}} + \underset{\text{water}}{2H_2O_{(l)}} \quad \Delta H = -890.3 \text{ kJ mol}^{-1}$$

The above reaction may be represented on an Enthalpy Profile Diagram as shown in Figure 21.4.

An **exothermic reaction** is a chemical reaction that produces heat. Since heat is lost to the surroundings, the enthalpy of the products is smaller than the enthalpy of the reactants.

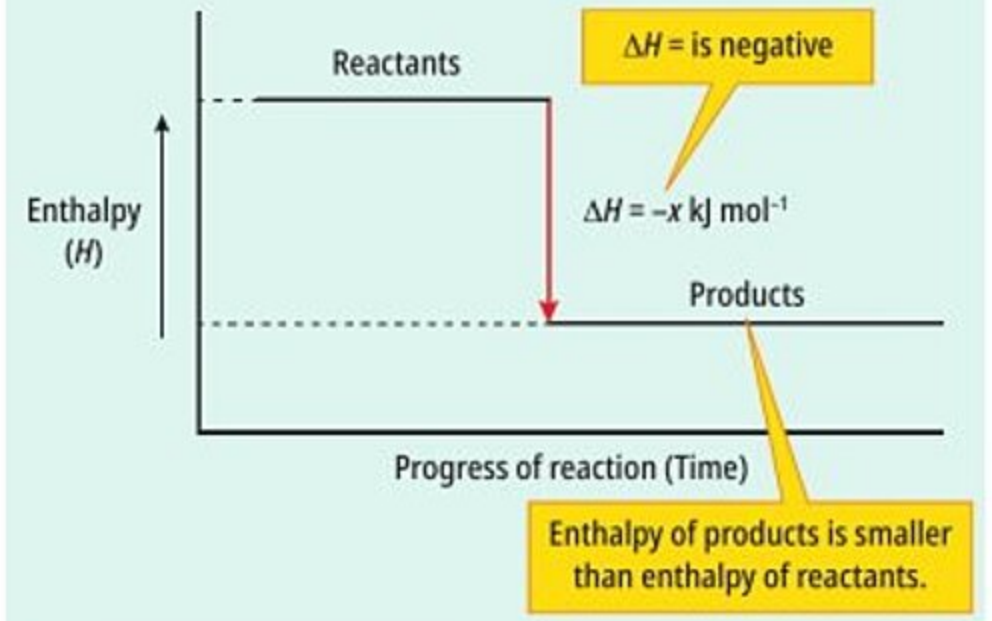


Figure 21.2 Enthalpy profile diagram for an exothermic reaction

Figure 21.3 The combustion of natural gas with oxygen in the air results in the formation of carbon dioxide and water.

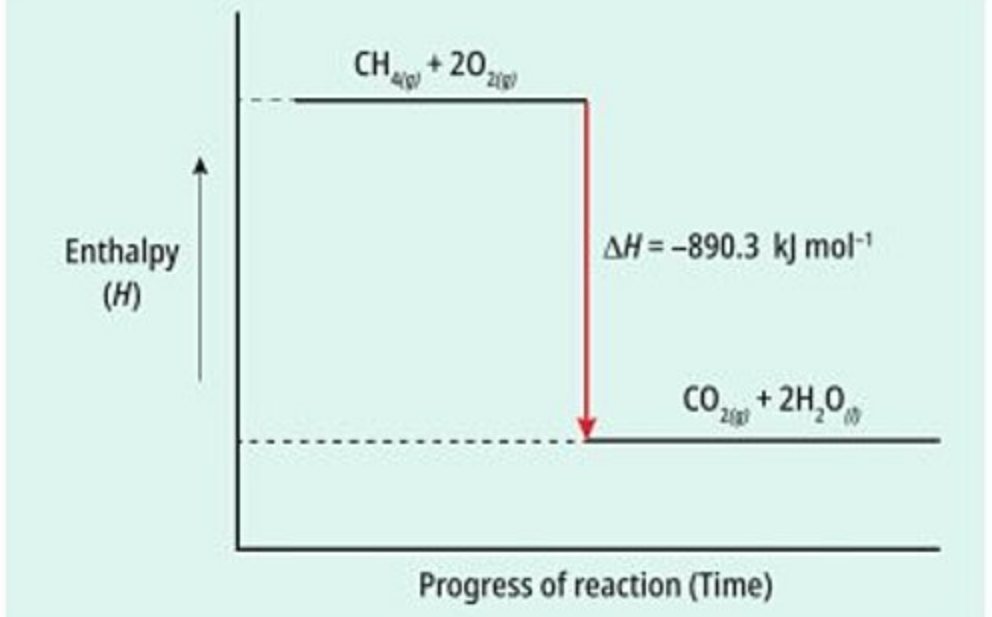


Figure 21.4 Enthalpy profile diagram for combustion of methane

(ii) Respiration. This is the biochemical process in which energy stored in glucose is released for use in cells. It occurs in all living cells. This 'burning' of glucose inside our bodies supplies us with the energy we need.

$$\underset{\text{glucose}}{C_6H_{12}O_{6(s)}} + \underset{\text{oxygen}}{6O_{2(g)}} \rightarrow \underset{\text{carbon dioxide}}{6CO_{2(g)}} + \underset{\text{water}}{6H_2O_{(l)}} \quad \Delta H = -2801 \text{ kJ mol}^{-1}$$

As this reaction involves oxygen gas, this process is also known as aerobic respiration. Anaerobic (without oxygen) respiration can also occur in cells, and also results in the release of energy.

(iii) Rusting. As you are aware, the rusting of iron is a very slow process, so it is not very obvious that it is an exothermic process. It may be described by the following equation:

$$\underset{\text{iron}}{4Fe_{(s)}} + \underset{\text{oxygen}}{3O_{2(g)}} \rightarrow \underset{\text{iron(III) oxide}}{2Fe_2O_{3(s)}} \quad \Delta H = -1{,}650 \text{ kJ mol}^{-1}$$

Another common exothermic reaction is the neutralisation process when acids and bases react. We will study this in more detail later on in this chapter.

Endothermic reactions

Not all chemical reactions give out heat. In some cases, a drop in temperature is observed when a chemical reaction occurs. In these cases, heat is taken in from the surroundings. You will notice the drop in temperature if you hold a beaker of water at room temperature and add sherbet to it. Heat is taken in from your hand. Such a reaction is called an **endothermic reaction**. ('Endon' is the Greek word for 'inside'.) An endothermic reaction is one that takes in heat.

An endothermic reaction is a chemical reaction that takes in heat. Since heat is taken in from the surroundings, the enthalpy of the products is greater than that of the reactants.

If you study Figure 21.5, you will see that the enthalpy of the products is greater than that of the reactants. In other words, heat is taken in when the reaction takes place.

Some examples of endothermic reactions are:

(i) Thermal decomposition

In some chemical reactions, heating a chemical causes it to break down into similar substances. The use of heat to break down a substance is called thermal decomposition.

Thermal decomposition is a chemical reaction in which heat is applied to a single compound to cause it to break down into two or more simple substances.

Since energy is absorbed in the form of heat, thermal decomposition reactions are almost always endothermic. (There are a few exceptions in the case of some explosives but these need not concern us in this course.)

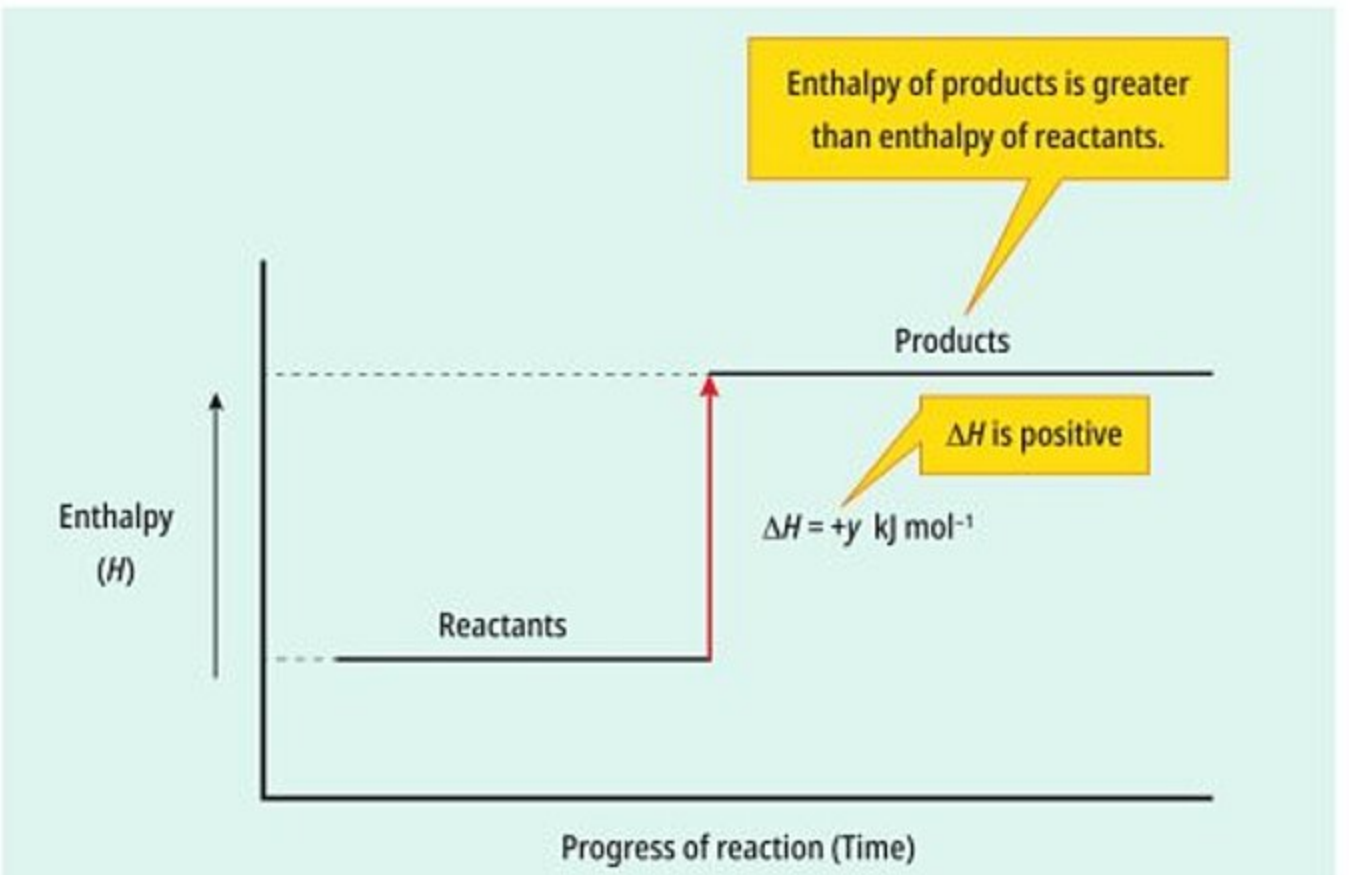


Figure 21.5 Enthalpy profile diagram for an endothermic reaction

An example of a thermal decomposition reaction is the decomposition of limestone (calcium carbonate) to lime (calcium oxide). Lime is used in agriculture and in the construction industry.

$$\underset{\text{limestone}}{CaCO_{3(s)}} \xrightarrow{\text{heat}} \underset{\text{lime}}{CaO_{(s)}} + CO_{2(g)} \quad \Delta H = +178 \text{ kJ mol}^{-1}$$

This reaction plays an important role in the manufacture of cement, Figure 21.6.

The enthalpy profile diagram for the thermal decomposition of limestone is shown in Figure 21.7.

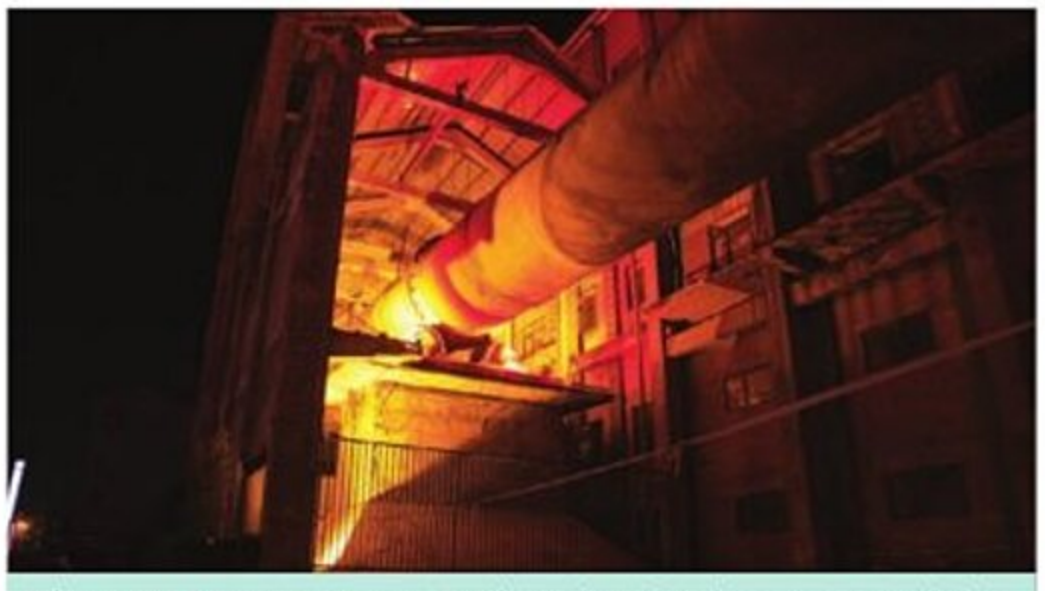


Figure 21.6 Limestone is placed in this large rotary kiln and is heated to convert it to lime. This endothermic reaction is important in the manufacture of cement.

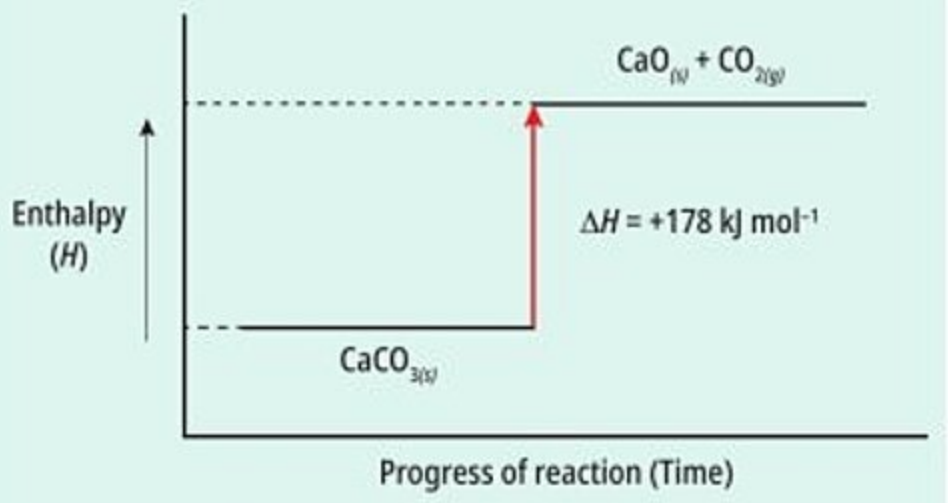


Figure 21.7 Enthalpy profile diagram for the decomposition of limestone to lime in the manufacture of cement.

Another example of a thermal decomposition reaction involves the use of sodium hydrogencarbonate (baking soda) in baking. When the sodium hydrogencarbonate is heated, the sodium hydrogencarbonate decomposes as follows

$$\underset{\substack{\text{sodium}\\\text{hydrogencarbonate}}}{2NaHCO_{3(s)}} \xrightarrow{\text{heat}} \underset{\substack{\text{sodium}\\\text{carbonate}}}{Na_2CO_{3(s)}} + H_2O_{(g)} + CO_{2(g)} \quad \Delta H = +129 \text{ kJ mol}^{-1}$$

The carbon dioxide gas formed gets trapped in the dough and this helps the dough to rise.

(ii) Photosynthesis

In Junior Cycle science, you learned that when photosynthesis takes place, energy is absorbed in the form of sunlight by plants to make glucose. Since energy is absorbed, photosynthesis is another example of an endothermic reaction.

$$6CO_{2(g)} + 6H_2O_{(l)} \xrightarrow{\text{light energy}} \underset{\text{glucose}}{C_6H_{12}O_{6(s)}} + 6O_{2(g)} \quad \Delta H = +2801 \text{ kJ mol}^{-1}$$

In photosynthesis, the chlorophyll in plants allows light energy from the Sun to be absorbed and converted into chemical energy. The chemical energy is stored in the chemical bonds of glucose, Figure 21.8.

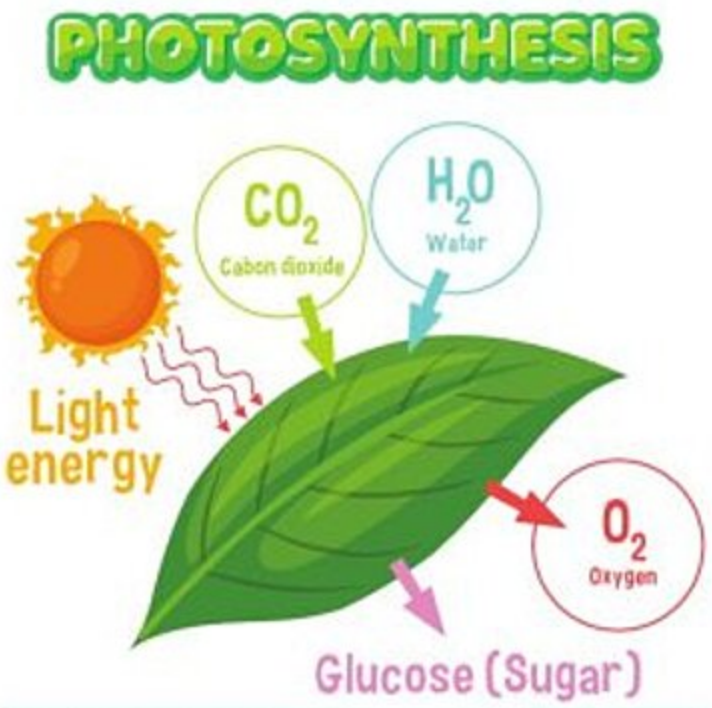


Figure 21.8 Photosynthesis is an example of an endothermic reaction.

Physical changes and enthalpy changes

So far we have been discussing chemical changes. A chemical change is a change that results in the formation of one or more new substances. You may recall that in Junior Cycle, you also learned about physical changes.

A **physical change** is a change that does not result in the formation of any new substance.

Changes of state also result in enthalpy changes. Changes of state are not classified as exothermic or endothermic reactions, since they are merely physical changes rather than chemical reactions. It is more correct to refer to them as exothermic or endothermic processes.

Some examples of physical changes are:

(i) Melting. When ice melts, energy is absorbed to overcome the intermolecular forces between the water molecules in the crystal lattice. It is found that 6.01 kJ of energy are absorbed for every mole of ice (18.02 g) that melts. This quantity is called the **enthalpy of fusion** of ice. 'Fusion' is just another word for melting.

$$H_2O_{(s)} \rightarrow H_2O_{(l)} \quad \Delta H_{fus} = +6.01 \text{ kJ mol}^{-1}$$

The **enthalpy of fusion** (ΔH_{fus}) is the energy absorbed when one mole of a solid melts to become a liquid at constant pressure.

(ii) Boiling. When water boils, energy is absorbed to overcome the intermolecular forces between the water molecules. It is found that 40.7 kJ of energy are absorbed for every mole of water that is converted to steam. This quantity is called the **enthalpy of vaporisation** of water.

$$H_2O_{(l)} \rightarrow H_2O_{(g)} \quad \Delta H_{vap} = +40.7 \text{ kJ mol}^{-1}$$

The **enthalpy of vaporisation** (ΔH_{vap}) is the energy absorbed when one mole of a liquid boils to become a gas at constant pressure.

Note that the enthalpy of vaporisation is higher than the enthalpy of fusion. This is because not only must the intermolecular forces between the water molecules be overcome, but also the particles must be fully separated in the gas.

Enthalpy of vaporisation can be demonstrated if you put a few drops of a volatile liquid such as ether or propanone on the back of your hand. You will feel a drop in temperature because the heat energy needed to change the liquid to a gas comes from your hand.

When steam is converted to water (condensation) this entire large amount of energy (40.7 kJ mol^{-1}) is released. A burn from steam can be more harmful than a burn from boiling water, Figure 21.9. Boiling water is never hotter than 100 ^{0}C but steam could be at much higher temperatures. If the hot steam condenses on your skin, the excess energy of the gaseous molecules is lost (in the form of heat) when they become a liquid.

Figure 21.9 A burn caused by steam is more severe than that caused by boiling water, since more heat is released when the hot steam condenses on skin.

(iii) Dissolving. In many cases, dissolving a salt in water is simply a physical change. For example, if sodium chloride is dissolved in water there is a slight fall in temperature and the solution is slightly cool to touch.

$$NaCl_{(s)} \rightarrow Na^{+}_{(aq)} + Cl^{-}_{(aq)} \quad \Delta H_{sol} = +3.9 \text{ kJ mol}^{-1}$$

However, if calcium chloride is dissolved in water there is a rise in temperature and the solution feels hot to touch.

$$CaCl_{2(s)} \rightarrow Ca^{2+}_{(aq)} + 2Cl^{-}_{(aq)} \quad \Delta H_{sol} = -81.3 \text{ kJ mol}^{-1}$$

Enthalpy of solution (ΔH_{sol}) is the enthalpy change when one mole of a solute dissolves in water to form an infinitely dilute solution at 25 °C and standard atmospheric pressure.

An 'infinitely dilute solution' means that the ions are well separated from each other in solution and do not interact with each other as they are surrounded by water molecules. In practice, this is achieved by dissolving a small number of grams of the salt in a fairly large volume of water (about 200 cm^3) to ensure a dilute solution. Then the temperature change is measured. By taking the volume of water into account and the mass of solute added, the heat of solution can be calculated. Since this experiment is not on our course, you need not worry about the details of how enthalpy of solution is measured in practice.

We have already stated that in many cases, dissolving a salt in water is simply a physical change. However, in other cases, when the substance is added to water, a chemical reaction may occur. We have already studied some of these reactions with water in Chapter 7.

Standard conditions for measuring enthalpy changes

Enthalpy changes for various chemical reactions are listed in databases around the world. Therefore, it is important that these values of enthalpy changes are measured under the same conditions. The conditions chosen by chemists are the normal conditions that are found in a science laboratory. These conditions are:

- **Standard temperature for measuring enthalpy changes** = 25 °C (298 K)
- **Standard pressure** = atmospheric pressure = 1.01325×10^5 Pa (SEC *Formulae and Tables* booklet)

Note that the standard temperature for enthalpy is different to the standard temperature that we met when discussing the properties of gases, i.e. standard temperature for gases = 273.15 K.

TEST YOURSELF: Attempt Questions 21.1 and W21.1.

21.3 Heat of combustion

The term *enthalpy of reaction* is a general term used for any type of chemical reaction. In some cases a different term is used to indicate the particular type of chemical reaction being considered. As already stated, a reaction in which a substance is burned is called a **combustion reaction**. Consider the reaction in which carbon is burned in oxygen to form carbon dioxide:

$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)} \qquad \Delta H = -394 \text{ kJ mol}^{-1}$$

The heat change in this reaction (–394 kJ mol^{-1}) is called the **heat of combustion** of the reaction. It is defined as follows:

> The **heat of combustion** of a substance is the heat change when one mole of the substance is completely burned in excess oxygen.

Note: In keeping with the syllabus documentation, the terms *heat* and *enthalpy* are used interchangeably in this textbook. The term *heat of combustion* may also be called *enthalpy of combustion*.

The phrase 'completely burned in excess oxygen' is important in the definition of heat of combustion. This is because some elements have more than one oxide, e.g.

$$C_{(s)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{(g)} \qquad \Delta H = -111 \text{ kJ mol}^{-1}$$

This value of ΔH is **not** the heat of combustion of carbon, since complete combustion of carbon in excess oxygen forms carbon dioxide, not carbon monoxide.

Another important phrase in the definition of heat of combustion is 'one mole'. Consider the thermochemical equation to describe what happens when butane from a gas cylinder is burned when using a gas cooker:

$$2C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(g)} \qquad \Delta H = -5754 \text{ kJ mol}^{-1}$$

Is –5754 kJ mol^{-1} the heat of combustion of butane? It is not since, by definition, the heat of combustion involves **one** mole of the substance being burned.

Therefore, the heat of combustion of butane is $-\frac{5754}{2} = -2877$ kJ mol^{-1}.

This may be represented by the following thermochemical equation:

$$C_4H_{10(g)} + 6\tfrac{1}{2}\,O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(g)}$$
$$\Delta H = -2877 \text{ kJ mol}^{-1}$$

Heats of combustion are accurately measured using an instrument called a bomb calorimeter. A calorimeter is any container used for the determination of heat changes. (The name comes from an old unit of energy called the calorie, 1 calorie = 4.18 joules.) As the bomb calorimeter is not on your course, we will not discuss the details of how it works. However, we will meet the name 'calorimeter' again, so remember this name!

Some examples of heats of combustion of various fuels are given in Table 21.1.

Fuel	Formula	Heat of combustion ΔH measured in kJ mol^{-1} at 25 °C
Methane	$CH_{4(g)}$	–890
Ethane	$C_2H_{6(g)}$	–1560
Propane	$C_3H_{8(g)}$	–2220
Butane	$C_4H_{10(g)}$	–2877
Hexane	$C_6H_{14(l)}$	–4194
Ethanol	$C_2H_5OH_{(l)}$	–1371
Carbon	$C_{(s)}$	–394
Hydrogen	$H_{2(g)}$	–286

Table 21.1 Heats of combustion of some fuels

21.1 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 19 in the Student Laboratory Notebook.

Student Experiment No. 19

To investigate the heat of combustion of a series of alcohols using spirit burners

Introduction

In this experiment, we will measure the amount of energy released when a certain mass of an alcohol is burned in air. The amount of heat will be measured by heating a known mass of water in a container made of copper. The container is called a calorimeter. Copper is usually used as it is a good conductor of heat. By measuring the temperature rise caused by heating a certain amount of water, we can calculate the heat of combustion of the alcohol.

The **heat of combustion** of a substance is the heat change when one mole of the substance is completely burned in excess oxygen. The heats of combustion of the first six primary alcohols are summarised in Table 21.2

Name of alcohol	Formula	Balanced equation for combustion	$\Delta H_{combustion}$
Methanol	CH_3OH	$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)}$ $\Delta H = -1452$ kJ mol^{-1}	–726 kJ mol^{-1}
Ethanol	C_2H_5OH	$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$ $\Delta H = -1367$ kJ mol^{-1}	–1367 kJ mol^{-1}
Propan-1-ol	C_3H_7OH	$2C_3H_7OH_{(l)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 8H_2O_{(l)}$ $\Delta H = -4042$ kJ mol^{-1}	–2021 kJ mol^{-1}
Butan-1-ol	C_4H_9OH	$C_4H_9OH_{(l)} + 6O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)}$ $\Delta H = -2676$ kJ mol^{-1}	–2676 kJ mol^{-1}
Pentan-1-ol	$C_5H_{11}OH$	$2C_5H_{11}OH_{(l)} + 15O_{2(g)} \rightarrow 10CO_{2(g)} + 12H_2O_{(l)}$ $\Delta H = -6662$ kJ mol^{-1}	–3331 kJ mol^{-1}
Hexan-1-ol	$C_6H_{13}OH$	$C_6H_{13}OH_{(l)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 7\ H_2O_{(l)}$ $\Delta H = -3984$ kJ mol^{-1}	–3984 kJ mol^{-1}

Table 21.2 Summary of thermochemical equations and heats of combustion for the first six primary alcohols

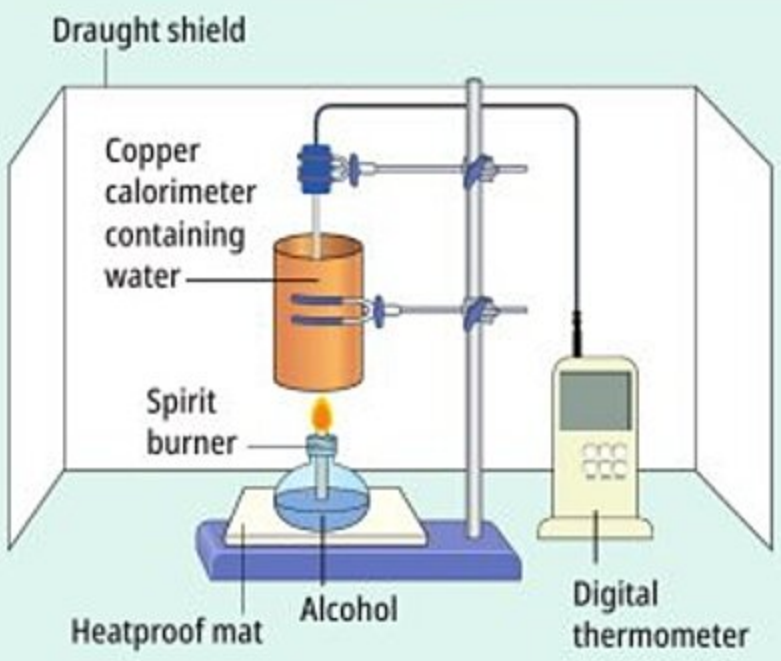


Figure 21.10 Measuring the heat of combustion of an alcohol

Key steps in procedure

- The apparatus is set up as shown in Figure 21.10.
- The copper calorimeter is clamped directly above the spirit burner.
- A draught shield is placed around the apparatus.

Explanation

- The purpose of the draught shield is to improve the accuracy of the experiment. In the lab, air currents can blow the flame of the burner sideways. This disperses the heat. We need to keep the heat from the burner concentrated on the calorimeter. Our calculations assume that all the heat from the burning alcohol is used to heat the water.
- The heatproof mat protects the surface of the bench in case the glass spirit-burner may crack due to heat generated by the burning wick.

Key steps in procedure (continued)

- A graduated cylinder is used to place a known volume (depending on the capacity of the calorimeter) of water in the copper calorimeter.
- Fill the spirit burner to about half its capacity with the alcohol being investigated.
- Place the cap on the spirit burner and find the total initial mass of the spirit burner and alcohol.

Explanation

- We need an exact volume of water to calculate the heat transferred to the water.
- We need to know the initial mass of the alcohol in order to calculate the mass of alcohol burned.
- We need to keep the cap on the spirit burner to avoid loss of alcohol by evaporation.

Key steps in procedure (continued)

- Place the spirit burner under the calorimeter, remove the cap and light the wick.
- Allow the alcohol to burn and heat the water.
- From time to time, stir the water gently using a glass rod.
- When the temperature has risen by a certain amount (e.g. 40 °C), extinguish the flame and replace the cap on the spirit burner.
- Find the new mass of the spirit burner and cap.

Explanation

- The water is stirred with the glass rod during heating to ensure even distribution of heat.
- We need to know the initial temperature of the water and the final temperature.
  The temperature rise will help us to calculate the heat transferred from the burning alcohol to the water.
- We need to find the new mass of the spirit burner and cap in order to find the mass of alcohol that has been burned.

Calculations

- The heat gained by the water in the combustion of the alcohol is calculated using the equation:

Heat gained = mass of water × specific heat capacity of water × rise in temperature of water
$= m \times c \times (t_2 - t_1)$.

m = mass of water in kg.

c = specific heat capacity of water in J kg^{-1} K^{-1}

$t_2 - t_1$ = temperature rise

The **specific heat capacity (c)** of a substance is the amount of heat required to raise the temperature of 1 kg of a substance by 1 K. For example, the specific heat capacity of water is 4200 J kg^{-1} K^{-1}. (This can also be written as 4.2 kJ kg^{-1} K^{-1}.) This means that it takes 4200 joules of heat to raise the temperature of 1 kg of water from, say, 19 °C to 20 °C.

In carrying out the experiment, we assume that all the heat produced by the burning alcohol goes towards the raising of the temperature of the water in the copper calorimeter.

- Knowing the heat liberated when a certain mass of alcohol was burned, it is then possible to calculate the amount of heat that would be liberated when one mole of the alcohol is completely burned in excess oxygen, i.e. the heat of combustion of the alcohol. The answer you get is an approximation and, therefore, may not be the one quoted in data books of heats of combustion.

When writing up an account of this experiment in your laboratory notebook, discuss the possible sources of error and steps that you took to ensure the accuracy of your results. These are outlined in the Laboratory Notebook accompanying this textbook

A sample calculation is given in Example 21.1.

Example 21.1

Question

A group of students performed an experiment to measure the heat of combustion of methanol. They used a copper calorimeter containing 80 cm^3 of water. The initial temperature of the water was 21.0 °C and the final temperature was 63.5 °C. The mass of the spirit burner and methanol before heating was 154.62 g and after heating was 154.01 g. Assuming that all the energy released by the burning alcohol went into heating the water, calculate the heat of combustion of methanol. The specific heat capacity of water is 4200 J kg^{-1} K^{-1}. Density of water is 1 g cm^{-3}.

Answer

Initial temperature of water: 21.0 °C

Final temperature of water: 63.5 °C

Initial mass of spirit burner and fuel: 154.62 g

Final mass of spirit burner and fuel: 154.01 g

Specific heat capacity of water: 4200 J kg^{-1} K^{-1}

Step 1

Calculate the mass of methanol burned.

Mass burned = mass before burning – mass after burning

= 154.62 g - 154.01 g

= 0.61 g

Step 2

Convert the mass of methanol to moles

$$\text{No. of moles methanol} = \frac{\text{Mass}}{\text{Relative molecular mass}}$$

$$= \frac{0.61}{32.042}$$

= 0.0190 mole

$1 \times C = 2 \times 12.01$	= 12.01
$4 \times H = 4 \times 1.008$	= 4.032
$1 \times O = 1 \times 16.00$	= 16.00
$M_r\ CH_3OH$	= 32.042

Step 3

Convert mass of water to kilograms.

80.0 cm^3 of water = 80.0 g = 0.08 kg

Step 4

Calculate the temperature rise.

Temperature rise = final temperature – initial temperature

= 63.5 °C - 21.0 °C

= 42.5 °C

Step 5

Calculate the heat absorbed by the water.

Heat gained = mass × specific heat capacity × rise in temperature

$= m \times c \times (t_2 - t_1)$

$= 0.08 \times 4200 \times 42.5$

= 14,280 J

= 14.28 kJ

Step 6

Calculate the heat of combustion in kJ per mole.

0.0190 mole of methanol releases 14.28 kJ

Therefore, 1 mole of methanol would release $\frac{14.28}{0.0190}$ kJ

= 751.58 kJ

Answer: Heat of combustion ΔH_{comb} = *–751.58 kJ mol^{-1}*

EXAM TIP!

The most common error in exams is for students to forget to convert grams of water to kilograms when substituting into the equation to calculate the heat gained. It is important to have the mass of the water heated in kg, since the units of specific heat capacity involve kg.

TEST YOURSELF: Attempt Questions 21.2 and W 21.2 –W21.4.

21.4 Bond enthalpy

Let us now consider what determines the value of ΔH for a particular reaction. Suppose we consider the combustion of methane:

$$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)} \qquad \Delta H = -890 \text{ kJ mol}^{-1}$$

As already discussed in Chapter 5, when a chemical reaction occurs, bonds are broken and new bonds are formed. Energy is required to break a bond and energy is released when a bond is formed. If we examine the left-hand side of the above equation, we see that four C–H bonds and two O=O bonds must be broken, Figure 21.11.

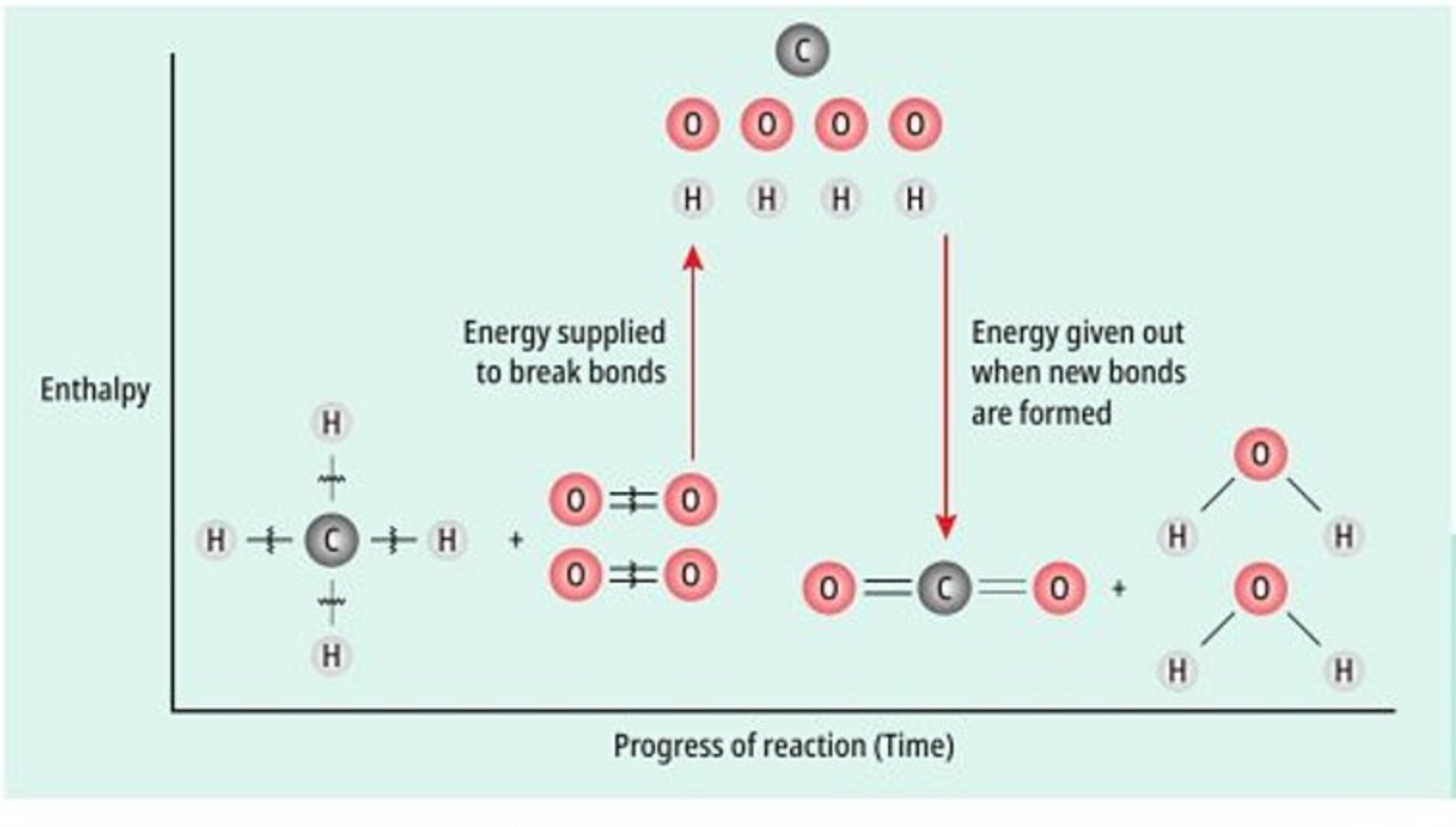


Figure 21.11 This diagram shows bond-breaking and bond-making for the combustion of methane in oxygen.

The energy involved in breaking bonds is called the **bond enthalpy** (also called **bond dissociation enthalpy** or **bond dissociation energy**) and is defined as follows:

Bond enthalpy is the average energy required to break one mole of a particular covalent bond and to separate the neutral atoms completely from each other.

Note that the definition always refers to the bond-breaking process. For example, consider the single covalent H – H bond in the H_2 molecule:

$$H_{2(g)} \rightarrow H_{(g)} + H_{(g)} \qquad \Delta H = +436 \text{ kJ mol}^{-1}$$

Note that we are breaking the single covalent bond between two hydrogen atoms in a molecule of hydrogen gas. Both hydrogen atoms then become separate hydrogen atoms. The bond enthalpy value tells us that it takes 436 kJ of energy to break one mole of H – H bonds.

Bond enthalpy values are measured from studying spectra of molecules and also from values of heats of reaction. They were used by Linus Pauling to draw up a table of electronegativity values (Chapter 6). Pauling realised that chemical bonds are like 'store rooms' for chemical energy. Some average bond enthalpy values are listed in Table 21.3. Bond enthalpy values tell you how much energy is needed to break different bonds. The higher the bond enthalpy value for a particular bond, the stronger the bond.

Bond	Average bond enthalpy value in kJ mol^{-1}
C–H	+412
C–C	+348
C=C	+614
C≡C	+839
O–H	+463
O=O	+498
C=O	+799
N≡N	+945

Table 21.3 Average bond enthalpy values for some bonds

- Note that bond enthalpy values are always given as bond enthalpy per mole of bonds broken.
- The same quantities of energy would be released when the bonds are formed.
- The + sign is placed before each average bond enthalpy value to emphasise that energy is needed to break bonds. In other words, bond breaking is an endothermic process.
- The reason that the bond enthalpy values in Table 21.3 are **average** values is because it is found that the bond enthalpy value for a particular bond can vary. For example, the energy to break the first C–H bond in methane is not the same as that required to break any of the other C–H bonds.

$CH_{4(g)} \rightarrow CH_{3(g)} + H_{(g)}$ $\Delta H = +435$ kJ mol^{-1}

$CH_{3(g)} \rightarrow CH_{2(g)} + H_{(g)}$ $\Delta H = +444$ kJ mol^{-1}

$CH_{2(g)} \rightarrow CH_{(g)} + H_{(g)}$ $\Delta H = +444$ kJ mol^{-1}

$CH_{(g)} \rightarrow C_{(g)} + H_{(g)}$ $\Delta H = +339$ kJ mol^{-1}

Therefore, average bond enthalpy of the methane C–H bond $= \frac{435 + 444 + 444 + 339}{4}$

$= \frac{1662}{4}$

$= 415.5$ kJ mol^{-1}

What decides whether a particular reaction is exothermic or endothermic overall?

Whether a particular reaction is exothermic or endothermic overall depends on bond enthalpy values.

- Breaking bonds in reactants always requires energy, i.e. it is always an endothermic process. The amount of energy needed depends on the bond enthalpies of the bond being broken.
- Forming bonds in products always releases energy, i.e. it is always an exothermic process. The amount of energy released depends on the bond enthalpies of the new bonds formed.

The ΔH for the overall reaction depends on the total energy needed to break bonds and the total energy released when bonds are formed.

ΔH *for* overall reaction = Total energy required to break bonds – total energy released in forming bonds.

- If more energy is released when forming bonds than is used to break the bonds ⇒ exothermic reaction.
- If more energy is used to break bonds than is released when new bonds are formed ⇒ endothermic reaction.

In short, the value of ΔH *for* a particular reaction is dependent on the amount of energy that is needed to break the bonds and the amount of energy that is liberated when the new bonds are formed.

We now study how we can analyse a given reaction involving covalent molecules to predict the value of ΔH for that reaction using average bond enthalpy values.

Example 21.2

Question

Methane reacts with oxygen to form carbon dioxide and water as shown in the following equation:

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$

Using the standard bond enthalpy values for the C–H bond, the O=O double bond, the C=O double bond and the O – H bond given in Table 21.3, calculate the enthalpy of reaction.

Answer

When answering questions of this type, it is helpful if you write out the equation in a similar form to that shown in Figure 21.12. This will help you to avoid mistakes in identifying bonds that are broken and bonds that are made when the reaction takes place.

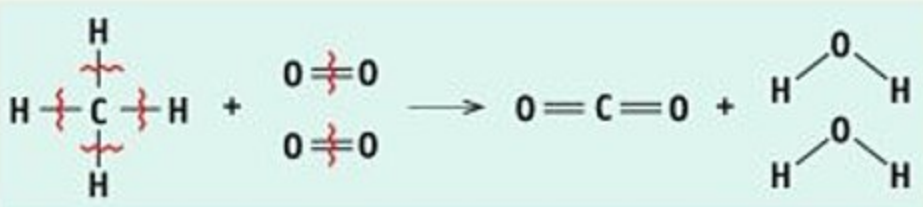


Figure 21.12 This type of diagram will help you to identify what bonds are broken and what bonds are made in a chemical reaction.

Note that Figure 21.12 is a simplified version of Figure 21.11. Use these types of simplified diagram to help you fill in the parts of Table 21.4 and Table 21.5. Be sure to show all your work so that you can maximise your marks in an exam.

Step 1

Calculate the energy needed to break all the bonds in the reactants.

Energy needed to break bonds (Reactants)

Bond and quantity	Bond enthalpy (kJ mol^{-1})	Total energy (kJ)
4 × C–H	412	4 × 412 = 1648
2 × O=O	498	2 × 498 = 996
	Total energy in	**2644**

Table 21.4 Calculate the total energy needed to break all the bonds in the reactants.

Step 2

Calculate the energy released when bonds are made in the products.

Energy released by making bonds (Products)

Bond and quantity	Bond enthalpy (kJ mol^{-1})	Total energy (kJ)
2 × C=O	799	2 × 799 = 1598
4 × O–H	463	4 × 463 = 1852
	Total energy out	**3450**

Table 21.5 Calculate the total energy released when all the bonds are made in the products.

Step 3

Calculate the enthalpy of reaction by substituting the values into the equation:

ΔH *for* overall reaction = Total energy required to break bonds – total energy released in forming bonds = 2644 – 3450 = –806 kJ

Answer: $CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$ $\Delta H = -806$ kJ mol^{-1}

TEST YOURSELF: Attempt Questions 21.3 and W 21.5–W21.9.

21.5 Enthalpy of neutralisation

We have already learned (Chapter 11) that neutralisation is the reaction between an acid and a base to form a salt and water.

e.g. $HCl + NaOH \rightarrow NaCl + H_2O$

We have also seen that the essential reaction taking place in this neutralisation reaction is:

$H^+ + OH^- \rightarrow H_2O$

Neutralisation reactions are nearly always exothermic. When discussing heat changes involved in neutralisation reactions, the term *enthalpy of neutralisation* is used. This term is defined as follows:

Enthalpy of neutralisation is the heat change when one mole of H^+ ions from an acid reacts with one mole of OH^- ions from a base.

Enthalpy of neutralisation is measured in kJ mol^{-1}. Consider the enthalpy of neutralisation of a number of strong acids and strong bases when dilute solutions of these acids and bases react together:

$HCl + NaOH \rightarrow NaCl + H_2O$ $\quad \Delta H = -57.1$ kJ mol^{-1}

$HCl + KOH \rightarrow KCl + H_2O$ $\quad \Delta H = -57.2$ kJ mol^{-1}

$HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$ $\quad \Delta H = -57.3$ kJ mol^{-1}

$HNO_3 + KOH \rightarrow KNO_3 + H_2O$ $\quad \Delta H = -57.3$ kJ mol^{-1}

You will observe that the enthalpy of neutralisation is almost the same in all cases. This is because, if we ignore 'spectator' ions, the essential reaction occurring is the same in all cases. ('Spectator' ions are ions that do not take part in the actual chemical change. They are unchanged on both the reactant and product sides of the chemical equation.)

For example, if we take a close look at the reaction between nitric acid and potassium hydroxide, we see that the reaction that occurs simply involves a proton and a hydroxide ion coming together to form water.

$H^+ + \cancel{NO_3^-} + \cancel{K^+} + OH^- \rightarrow \cancel{K^+} + \cancel{NO_3^-} + H_2O$

$H^+ + OH^- \rightarrow H_2O$ $\quad$ **$\Delta H = -57$ kJ mol^{-1}**

However, consider the reaction between a strong acid and a weak base or between a weak acid and a strong base:

$HCl + NH_4OH \rightarrow NH_4Cl + H_2O$ $\quad \Delta H = -52.2$ kJ mol^{-1}

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$ $\quad \Delta H = -55.2$ kJ mol^{-1}

When either a weak acid or a weak base is involved, the numerical value of ΔH is usually less than 57 kJ mol^{-1}. This is because weak acids and weak bases do not fully dissociate in water. For complete neutralisation to occur and form one mole of water, the weak acid or base must become fully dissociated. This dissociation requires energy, i.e. it is endothermic. Therefore, the heat released will be less than 57 kJ since a certain quantity of heat is required to cause complete dissociation of the acid or base.

21.2 Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 20 in the Student Laboratory Notebook.

Student Experiment No. 20

To determine the enthalpy of reaction for a neutralisation reaction

Introduction

In this experiment, a known number of moles of hydrochloric acid is mixed with an equal number of moles of sodium hydroxide in an insulated container. The rise in temperature of the mixture is then measured and, from this, the enthalpy of reaction is calculated.

In order to get a significant temperature rise, the solutions of HCl and NaOH that are used in this experiment are more concentrated (1 M) than those you used in carrying out titrations (0.1 M). Therefore, great care must be taken when handling these solutions. They must not be allowed to come in contact with your skin or eyes. As always, safety glasses should be worn throughout the experiment. The corrosive symbol on this page is important!

Key steps in procedure

- Using a graduated cylinder, a known volume of hydrochloric acid solution is placed in a polystyrene cup, Figure 21.13.
- The same volume of sodium hydroxide of the same concentration is placed in a second polystyrene cup.
- The volumes and concentrations of HCl and NaOH used are recorded.
- Both solutions are allowed to stand until they are at the same temperature.
- The temperature of each solution is recorded.

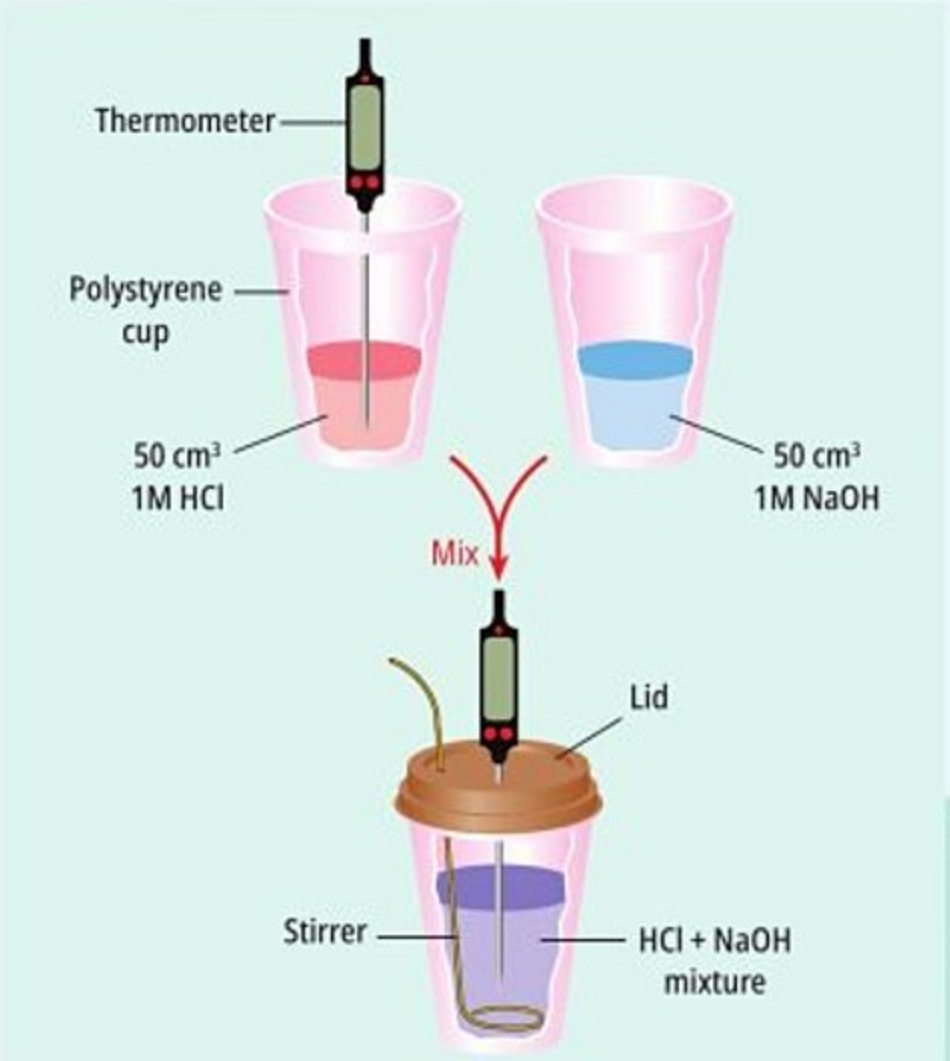


Figure 21.13 Measuring the enthalpy of reaction for the neutralisation reaction between hydrochloric acid and sodium hydroxide

- The sodium hydroxide solution is quickly added to the hydrochloric acid solution and care is taken to avoid any loss of liquid due to splashing.
- A lid is immediately placed on the polystyrene cup in which the two solutions have been mixed.
- The solution is stirred continuously.
- The maximum temperature reached by the mixture is recorded.

Observation

- A rise in temperature is observed.

Explanation

- More concentrated solutions of HCl and NaOH are used than were used in titrations in order to obtain a significant temperature rise in this experiment. If 0.1 M HCl and 0.1 M NaOH were used, the temperature rise would be small and would be difficult to accurately measure.

Calculations

- The heat given out in the reaction is calculated using the equation:

Heat given out = mass × specific heat capacity × rise in temperature
$= m \times c \times (t_2 - t_1)$.

m = mass of solution in kg.

c = specific heat capacity of solution in J kg^{-1} K^{-1}

$t_2 - t_1$ = temperature rise

In carrying out the experiment we assume that all the heat generated goes towards the raising of the temperature of the solution and that no heat is absorbed by the plastic container, i.e. the plastic container has negligible heat capacity.

Knowing the heat liberated when the number of moles of acid used was neutralised, it is now possible to calculate the amount of heat that would be liberated when one mole of the acid is neutralised, i.e. the enthalpy of reaction for the neutralisation of 1 mole of HCl by NaOH.

In carrying out the calculations the following points are worth noting:

In general, it is assumed that the density of the solution is the same as the density of water, i.e. that 100 cm^3 of the solution have a mass of 100 g or 0.1 kg.

You will always be given the specific heat capacity of the solution, e.g. when carrying out the calculations for the above experiment, the specific heat capacity of the solution is 4060 J kg^{-1} K^{-1}.

If the acid and base are at two different temperatures at the beginning of the experiment, use the **average** value when carrying out calculations.

EXAM TIP!

The most common error in exams is for students to forget to convert grams to kilograms when substituting into the above equation. It is important to have the mass of the solution in kg since the units of specific heat capacity involve kg.

The answer you get may not be the one quoted in data books of heats of reaction for the reaction between hydrochloric acid and sodium hydroxide. When writing up an account of this experiment in your laboratory notebook, discuss the possible sources of error and steps that you took to ensure the accuracy of your results. These are outlined in the Laboratory Notebook accompanying this textbook.

A Folens video of this Student Experiment is available online

The method of calculating the enthalpy of reaction for a neutralisation reaction is shown in Example 21.3.

Example 21.3

Question

A student carried out an experiment to measure the enthalpy of neutralisation of nitric acid by sodium hydroxide in a container made of plastic of negligible specific heat capacity. She used 100 cm^3 of 1.0 M nitric acid and 100 cm^3 of 1.0 M sodium hydroxide. The initial temperature of both of the solutions was 15.6 °C and the final temperature of the solution was 22.4 °C.

Given that the specific heat capacity of the solution is 4080 J kg^{-1} K^{-1}, calculate the enthalpy of neutralisation. (Assume that the density of the solution is 1 g cm^{-3}.)

Answer

Step 1

Convert grams to kg.

Mass of solution = 200 g = 0.2 kg.

Step 2

Calculate the temperature rise.

Temperature rise = 22.4 – 15.6 = 6.8 °C

Step 3

Calculate the heat given out.

Specific heat capacity = 4080 J kg^{-1} K^{-1}

Heat given out = mass × specific heat capacity × temp rise

= 0.2 × 4080 × 6.8

= 5548.8 joules

Step 4

Calculate the number of moles of acid that were neutralised.

Number of moles of HNO_3 that were neutralised = $\frac{\text{volume} \times \text{molarity}}{1000} = \frac{100 \times 1}{1000} = 0.1$

Step 5

Calculate the enthalpy of reaction.

0.1 mole of HNO_3 that is neutralised gives 5548.8 joules of heat

Therefore, 1 mole of HNO_3 that is neutralised gives 5548.8 × 10 = 55,488 J = 55.488 kJ of heat

Since for HNO_3, 1 mole of acid gives 1 mole of H^+ ions

∴ Enthalpy of neutralisation is –55.488 kJ mol^{-1}

i.e. $HNO_3 + NaOH \rightarrow NaNO_3 + H_2O$ $\quad \Delta H = -55.488$ kJ mol^{-1}

Answer: Enthalpy of neutralisation = –55.488 kJ mol^{-1}

If you use a diprotic acid such as sulfuric acid, you must take care in the calculations when determining the enthalpy of neutralisation, since one mole of acid gives **two** moles of H^+ ions,

e.g. $H_2SO_4 + 2NaOH \rightarrow Na_2SO_4 + 2H_2O$.

This is illustrated in Example 21.4.

» Study Example 21.4 in the online resources.

Example 21.5

Question

In an experiment to measure the enthalpy of reaction for the reaction between sodium hydroxide and hydrochloric acid, a student added 50 cm^3 of 1.0 M HCl solution to the same volume of 1.0 M NaOH solution in a polystyrene foam cup.

Calculate the total number of moles of acid neutralised in this experiment.

Taking the total heat capacity of the reaction mixture used in this experiment as 420 J K^{-1}, calculate the heat released in the experiment if a temperature rise of 6.7 °C was recorded.

Hence, calculate the enthalpy of reaction for $NaOH + HCl \rightarrow NaCl + H_2O$ [LCH]

Answer

Step 1

Calculate the number of moles of acid neutralised.

$$\text{Number of moles of HCl} = \frac{\text{volume} \times \text{molarity}}{1000} = \frac{50 \times 1}{1000} = 0.05 \text{ moles}$$

Step 2

Calculate the heat given out in the reaction.

Heat given out = Heat capacity × Rise in temperature

$= C \times (t_2 - t_1)$

$= 420 \times 6.7$

$= 2814$ joules

$= 2.814$ kJ

Step 3

Calculate the heat given out by one mole of HCl.

0.05 mol of HCl releases 2.814 kJ when neutralised

=> 1 mol would release $\frac{2.814}{0.05}$ kJ when neutralised = 56.28 kJ

i.e. the enthalpy of reaction is –56.28 kJ mol^{-1}

Answer: Enthalpy of reaction = –56.28 kJ mol^{-1}

In some cases, you may not be given the **specific heat capacity** of the solution but rather given the **heat capacity** of the overall system. The symbol for heat capacity is **C**. The heat capacity of an object is the amount of heat needed to change its temperature by 1 K.

Heat given out = heat capacity × rise in temperature = $C \times (t_2 - t_1)$.

EXAM TIP!

Remember to include the negative sign when writing down the final answer!

21.6 Enthalpy of formation

Sometimes chemists need to know the amount of energy absorbed or released when a compound is formed from its elements, e.g. the amount of energy released when water is formed from hydrogen and oxygen. Knowledge of this energy is very important when designing fuel cells as sources of power, Figure 21.14. The bus is powered by the reaction between hydrogen and oxygen to form water. We will be discussing fuel cells in more detail in Chapter 22.

TEST YOURSELF: Attempt Questions 21.4 and W21.10 –W21.12.

Figure 21.14 The reaction between hydrogen and oxygen to form water releases energy. The energy released is used to provide the power needed by this bus.

This enthalpy change that takes place when a compound is formed from its elements is called the enthalpy of formation and is defined as follows:

> The **enthalpy of formation** of a compound is the heat change that takes place when one mole of a compound in its standard state is formed from its elements in their standard states.

The **standard state** of an element or compound is its normal form at **25 °C** and at normal atmospheric pressure. (Another reminder! Do not confuse this temperature with the standard temperature that we met when discussing the properties of gases, i.e. standard temperature for gases = 273.15 K.) Thus, the standard state of oxygen is the gaseous state, that of water is the liquid state, and that of magnesium is the solid state – because these are the states in which these substances exist at 25 °C and standard pressure.

We will use water as an example to illustrate the concept of heat of formation. The heat of formation of water is found to be –285.8 kJ mol^{-1}. This may be represented as follows:

$$H_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \rightarrow H_2O_{(l)} \qquad \Delta H = -285.8 \text{ kJ mol}^{-1}$$

Note that one mole of water in its normal liquid state is formed in this reaction.

The following equation does **not** represent the heat of formation of water:

$$H_{2(g)} + \tfrac{1}{2}\, O_{2(g)} \rightarrow H_2O_{(g)} \qquad \Delta H = -241.8 \text{ kJ mol}^{-1}$$

This is because the water formed in the second equation above is in the gaseous state. At 25 °C the normal state of water is liquid.

Similarly, the following equation does not represent the heat of formation of water:

$$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)} \qquad \Delta H = -571.6 \text{ kJ mol}^{-1}$$

This is because the above equation shows the heat change that takes place when **two** moles of water are formed from its elements.

The heats of formation of most compounds have negative values of ΔH. The reason for this is that energy is given out when the compound is formed from its elements, Table 21.6. We would expect this since compounds are generally more stable than the elements from which they are formed.

Compound	Heat of formation ΔH measured in kJ mol^{-1}
$CH_{4(g)}$	–74.9
$C_2H_{6(g)}$	–84.7
$C_2H_5OH_{(l)}$	–278
$CO_{2(g)}$	–394
$NH_{3(g)}$	–46.2
$H_2O_{(l)}$	-285.8

Table 21.6 Heats of formation of some compounds

By definition, **enthalpy of formation** of a compound is the heat change that takes place when one mole of a compound in its standard state is formed from its elements in their standard states. Since an element in its standard state is already in that form, no formation is required, so the enthalpy change is zero. In short, the enthalpy of formation of any element in its standard state is zero.

A common error in exams is for students to write the heat of formation equations incorrectly. Study the following examples carefully, and note that in some cases it is necessary to introduce fractions in order to have 1 mole on the right of the equation:

$2C_{(s)} + H_{2(g)} \rightarrow C_2H_{2(g)}$ $\quad \Delta H = +227 \text{ kJ mol}^{-1}$

$\frac{1}{2} N_{2(g)} + 1\frac{1}{2} H_{2(g)} \rightarrow NH_{3(g)}$ $\quad \Delta H = -46 \text{ kJ mol}^{-1}$

$\frac{1}{2} H_{2(g)} + C_{(s)} + \frac{1}{2} N_{2(g)} \rightarrow HCN_{(g)}$ $\quad \Delta H = +130 \text{ kJ mol}^{-1}$

$3C_{(s)} + 1\frac{1}{2} H_{2(g)} + \frac{1}{2} N_{2(g)} \rightarrow C_3H_3N_{(g)}$ $\quad \Delta H = +194.5 \text{ kJ mol}^{-1}$

EXAM TIP!

When writing enthalpy of formation equations, always make sure you have one mole of product on the right-hand side of the equation!

21.7 Hess's Law

Imagine that you are climbing a mountain and that there are various paths to reach the top of the mountain. Regardless of what path you take, you will reach the same height at the top of the mountain. Germain Hess, Figure 21.15, discovered something similar about heat changes in chemical reactions.

Hess studied the heat changes involved in a wide variety of different chemical reactions. He found that the quantity of heat produced in going from one substance to another was the same no matter what route was taken. In 1840 he announced his results in what is now called Hess's Law:

In other words, the amount of heat liberated or absorbed in a chemical reaction is the same whether the reaction takes place in one or in several steps, Figure 21.16.

Consider the routes for converting carbon and oxygen to carbon dioxide, Figure 21.17.

Route 1: $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H_1 = -394 \text{ kJ mol}^{-1}$

Route 2: $C_{(s)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{(g)}$ $\quad \Delta H_2 = x \text{ kJ mol}^{-1}$

Route 3: $CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$ $\quad \Delta H_3 = -283 \text{ kJ mol}^{-1}$

In Route 1, carbon is converted directly to carbon dioxide ($\Delta H_1 = -394$ kJ mol^{-1}). In Route 2, carbon monoxide is first formed ($\Delta H_2 = x$ kJ mol^{-1}). In the next step the carbon monoxide is further oxidised to carbon dioxide ($\Delta H_3 = -283$ kJ mol^{-1}).

Figure 21.15

Germain Hess
(1802–1850)

Germain Hess was born in Geneva and became professor of chemistry in St Petersburg University, Russia. He is known as the founder of thermochemistry, as he measured the heat changes that took place in many chemical reactions.

Hess's Law states that if a chemical reaction takes place in a number of stages, the sum of the heat changes in the separate stages is equal to the heat change if the reaction is carried out in one stage.

Figure 21.16 Diagrammatic representation of Hess's Law

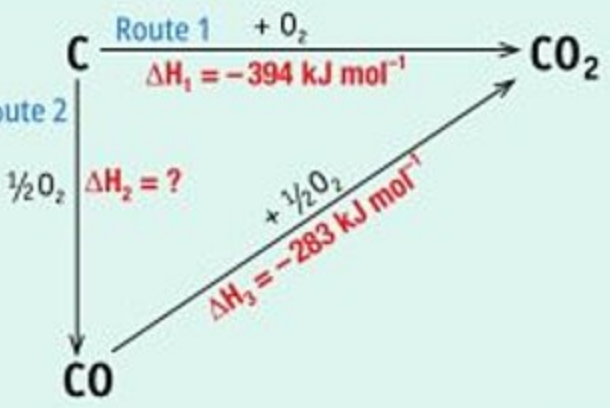


Figure 21.17 Hess's Law may be used to calculate the unknown enthalpy of reaction.

According to Hess's Law, the heat change for the single-step reaction is the same as the heat change for the two-step reaction.

i.e. $\Delta H_1 = \Delta H_2 + \Delta H_3$

$-394 = x - 283$

$x = -394 + 283 = -111$ kJ mol^{-1}

i.e. $C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$ $\Delta H_2 = -111$ kJ mol^{-1}

Thus, Hess's Law may be used to indirectly find the value of the enthalpy of reaction of a chemical reaction that may be difficult to measure directly in the laboratory. For example, it is difficult to measure experimentally the heat of formation of CO, since some CO_2 is also formed. However, the value may be calculated very accurately using Hess's Law.

In short, Hess's Law is very useful in chemistry because:

- Using Hess's Law, we can use enthalpy values that we **can** measure in the lab to calculate enthalpy values that we **cannot** measure in the lab.
- Therefore, it gives us a method for finding an enthalpy change **indirectly**.

Hess's Law is really just a re-statement of the more general Law of Conservation of Energy as applied to heat changes involved in chemical reactions.

The relationship between Hess's Law and the Law of Conservation of Energy is often illustrated in a simple energy profile diagram as shown in Figure 21.18. This energy profile is another way of representing the cycle type of diagram show in Figure 21.17.

The **Law of Conservation of Energy** states that energy cannot be created or destroyed but can only be converted from one form of energy into another.

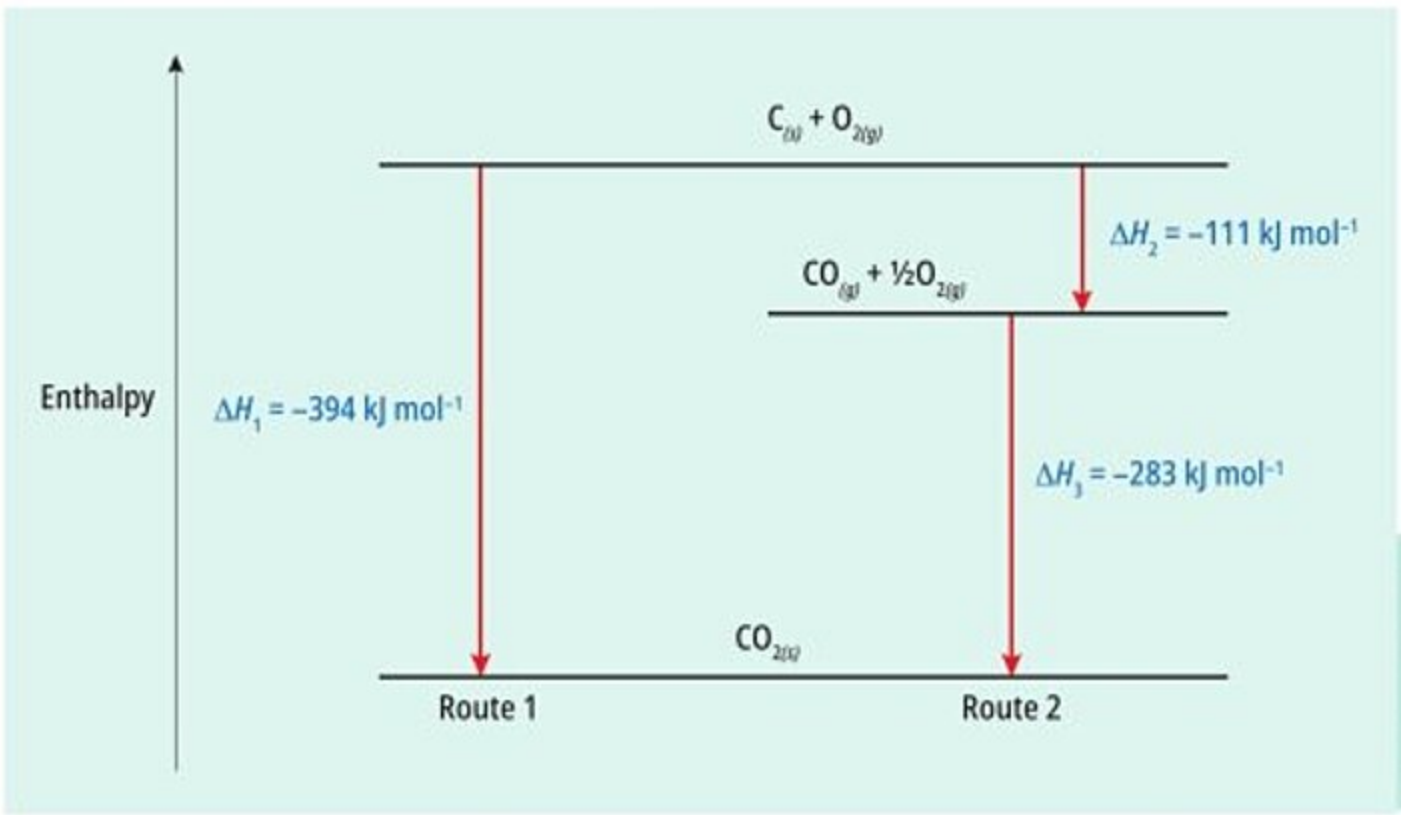


Figure 21.18 This energy profile diagram emphasises the relationship between Hess's Law and the Law of Conservation of Energy.

The great usefulness of Hess's Law is that it allows thermochemical equations to be added, subtracted, multiplied or divided to calculate unknown heats of reaction. For this reason, it is one of the most useful laws in thermochemistry.

We will now look at some examples of Hess's Law calculations to help you gain skills in carrying them out. When solving problems using Hess's Law, you are advised to approach them in a systematic fashion as shown in the examples that follow. If you approach the problem in a haphazard fashion you could end up 'going around in circles'.

Example 21.6

Question

Calculate the heat of formation of methane from the following data:

$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393$ kJ mol^{-1}

$H_{2(g)} + ½\ O_{2(g)} \rightarrow H_2O_{(g)}$ $\Delta H = -286$ kJ mol^{-1}

$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H = -879$ kJ mol^{-1} [LCH]

Answer

In this example we are asked to calculate the heat of formation of a compound using other heats of formation and one enthalpy of reaction

Step 1

Write down the equation you require. We need to write the equation for the heat of formation of methane. Thus, one mole of methane must be on the right-hand side of the equation. The elements from which methane is formed must be on the left-hand side of the equation. The equation must be balanced. The required equation is:

$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H = ?$

We must now build up each part of this equation (i.e. C, $2H_2$ and CH_4) using the given equations (a), (b) and (c) above.

Step 2

Introduce C. [C is in (a) above.]

(a) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393$ kJ mol^{-1}

Step 3

Introduce $2H_2$. We have H_2 in (b) above Therefore, multiply (b) by 2. Remember to also multiply ΔH by 2.

(b) × 2: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ $\Delta H = -572$ kJ mol^{-1}

Step 4

Get the left-hand side of the required equation by adding (a) to the above equation:

(a) $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}$ $\Delta H = -393$ kJ mol^{-1}

(b) × 2: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(g)}$ $\Delta H = -572$ kJ mol^{-1}

(d) $C_{(s)} + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H = -965$ kJ mol^{-1}

Step 5

Introduce CH_4. We have CH_4 on the left-hand side of equation (c). We need it on the right-hand side of the required equation in the box above. Therefore, reverse equation (c), remembering to also reverse the sign of ΔH.

(c) reversed: $CO_{2(g)} + 2H_2O_{(g)} \rightarrow CH_{4(g)} + 2O_{2(g)}$ $\Delta H = +879$ kJ mol^{-1}

Step 6

Now add (c) reversed to (d) above:

(d) $C_{(s)} + 2H_{2(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)}$ $\Delta H = -965$ kJ mol^{-1}

(c) reversed: $CO_{2(g)} + 2H_2O_{(g)} \rightarrow CH_{4(g)} + 2O_{2(g)}$ $\Delta H = +879$ kJ mol^{-1}

$C_{(s)} + 2H_{2(g)} + \cancel{2O_{2(g)}} + \cancel{CO_{2(g)}} + \cancel{2H_2O_{(g)}} \rightarrow \cancel{CO_{2(g)}} + \cancel{2H_2O_{(g)}} + CH_{4(g)} + \cancel{2O_{2(g)}}$ $\Delta H = -86$ kJ mol^{-1}

i.e. $C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}$ $\Delta H = -86$ kJ mol^{-1}

Answer: $\Delta H = -86$ kJ mol^{-1}

Example 21.7

Question

Calculate the enthalpy of reaction of the following reaction:

$2H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(g)} + 2H_2O_{(l)}$ $\Delta H = ?$

You are given the following heats of formation:

(a) $H_{2(g)} + S_{(s)} \rightarrow H_2S_{(g)}$ $\Delta H = -21$ kJ mol^{-1}

(b) $S_{(s)} + O_{2(g)} \rightarrow SO_{2(g)}$ $\Delta H = -297$ kJ mol^{-1}

(c) $H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\Delta H = -286$ kJ mol^{-1}

Answer

Note that in this example we are asked to calculate the enthalpy of reaction using heats of formation of reactants and products.

Step 1

The required equation is:

$2H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)}$ $\Delta H = ?$

Step 2

Introduce $2H_2S$ by reversing (a) and multiplying by 2.

(a) reversed: $H_2S_{(g)} \rightarrow H_{2(g)} + S_{(s)}$ $\Delta H = +21$ kJ mol^{-1}

(a) rev × 2: $2H_2S_{(g)} \rightarrow 2H_{2(g)} + 2S_{(s)}$ $\Delta H = +42$ kJ mol^{-1}

Step 3

Introduce $SO_{2(g)}$ by reversing (b).

(b) reversed: $SO_{2(g)} \rightarrow S_{(s)} + O_{2(g)}$ $\Delta H = +297$ kJ mol^{-1}

Step 4

Add (a) rev × 2 to (b) reversed.

(a) rev × 2: $2H_2S_{(g)} \rightarrow 2H_{2(g)} + 2S_{(s)}$ $\Delta H = +42$ kJ mol^{-1}

(b) reversed: $SO_{2(g)} \rightarrow S_{(s)} + O_{2(g)}$ $\Delta H = +297$ kJ mol^{-1}

(d): $2H_2S_{(g)} + SO_{2(g)} \rightarrow 2H_{2(g)} + 3S_{(s)} + O_{2(g)}$ $\Delta H = +339$ kJ mol^{-1}

Step 5

We already have 3S on the right-hand side of the equation. Therefore, the only remaining item to be introduced is the $2H_2O$. This is done by multiplying (c) by 2 and adding it to (d).

(c) × 2: $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$ $\Delta H = -572$ kJ mol^{-1}

(d): $2H_2S_{(g)} + SO_{2(g)} \rightarrow 2H_{2(g)} + 3S_{(s)} + O_{2(g)}$ $\Delta H = +339$ kJ mol^{-1}

Add: $\cancel{2H_{2(g)}} + \cancel{O_{2(g)}} + 2H_2S_{(g)} + SO_{2(g)} \rightarrow 2H_2O_{(l)} + \cancel{2H_{2(g)}} + 3S_{(s)} + \cancel{O_{2(g)}}$

i.e. $2H_2S_{(g)} + SO_{2(g)} \rightarrow 3S_{(s)} + 2H_2O_{(l)}$ $\Delta H = -233$ kJ mol^{-1}

Answer: $\Delta H = -233$ kJ mol^{-1}

As we come near to completing our study of thermochemistry, note that the change in enthalpy for particular processes can be determined in three ways:

1. By measurement in the laboratory
2. Using values of bond enthalpy data
3. Using standard heats of formation of reactants and products.

TEST YOURSELF: Attempt Questions 21.5 and W21.13 –W21.22.

» Study SEC exam question 21.8 and model answer in the online resources.

21.8 Trends in ΔH values for complete combustion of hydrocarbons and primary alcohols

As discussed in Chapter 23 (see the *Assessment and Exam Guide*), a hydrocarbon is a compound that contains carbon and hydrogen only. In this course, we need to know how to write balanced equations for the complete combustion of hydrocarbons and primary alcohols. Let's begin by studying the complete combustion of some hydrocarbons.

Complete combustion of hydrocarbons

Complete combustion means that when a hydrocarbon burns in oxygen, there is sufficient oxygen present to produce only carbon dioxide and water as products. In other words, all the carbon atoms in the hydrocarbon are oxidised to carbon dioxide and all the hydrogen atoms are oxidised to water. On the contrary, incomplete combustion means that there is insufficient oxygen present. When insufficient oxygen is present, carbon monoxide (CO) and carbon (soot) are formed.

The balanced equations for the complete combustion of the first six alkanes are shown in Table 21.7. You are expected to construct these balanced equations yourself and you will get plenty of practice in balancing equations in the workbook accompanying this textbook. Once you get in the practice, balancing these equations will be a piece of cake!

Name of alcohol	Formula	Balanced equation for complete combustion		$\Delta H_{combustion}$
Methane	CH_4	$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H = -890$ kJ mol^{-1}	–890 kJ mol^{-1}
Ethane	C_2H_6	$2C_2H_{6(g)} + 7O_{2(g)} \rightarrow 4CO_{2(g)} + 6H_2O_{(l)}$	$\Delta H = -3120$ kJ mol^{-1}	–1560 kJ mol^{-1}
Propane	C_3H_8	$C_3H_{8(g)} + 5O_{2(g)} \rightarrow 3CO_{2(g)} + 4H_2O_{(l)}$	$\Delta H = -2220$ kJ mol^{-1}	–2220 kJ mol^{-1}
Butane	C_4H_{10}	$2C_4H_{10(g)} + 13O_{2(g)} \rightarrow 8CO_{2(g)} + 10H_2O_{(l)}$	$\Delta H = -5754$ kJ mol^{-1}	–2877 kJ mol^{-1}
Pentane	C_5H_{12}	$C_5H_{12(g)} + 8O_{2(g)} \rightarrow 5CO_{2(g)} + 6H_2O_{(l)}$	$\Delta H = -3535$ kJ mol^{-1}	–3535 kJ mol^{-1}
Hexane	C_6H_{14}	$2C_6H_{14(g)} + 19O_{2(g)} \rightarrow 12CO_{2(g)} + 14H_2O_{(l)}$	$\Delta H = -8326$ kJ mol^{-1}	–4163 kJ mol^{-1}

Table 21.7 Balanced equations and heats of combustion for the complete combustion of saturated hydrocarbons up to C6

Note the following from Table 21.7:

- There is a steady increase in the quantity of heat (enthalpy of combustion) as the number of carbon atoms increases.
- This steady increase in the size of $\Delta H_{combustion}$ is almost linear as shown in Figure 21.19.

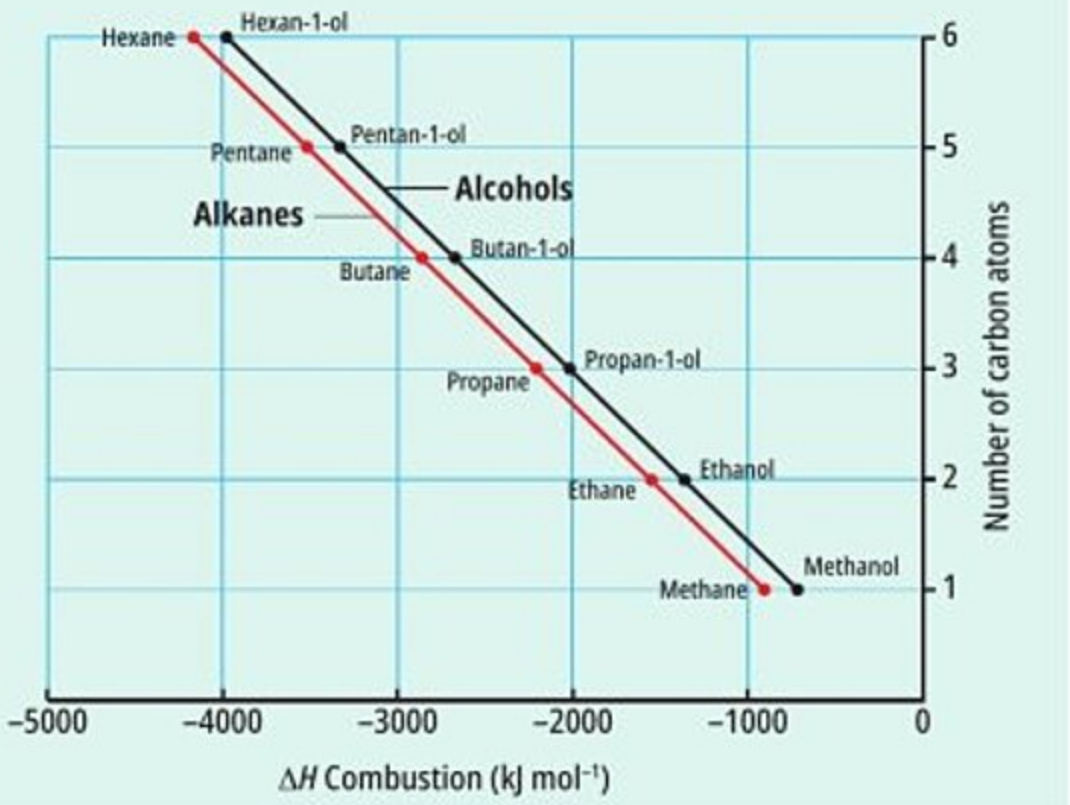


Figure 21.19 Graph of enthalpy of combustion *versus* number of carbon atoms for the first six alkanes and the first six primary alcohols.

Why is there an increase in the size of the enthalpy of combustion for the alkanes every time a CH_2 unit is added?

- Every time you move from one alkane to the next (methane to ethane, ethane to propane) you add one CH_2 group.
- The larger alkane of a consecutive pair has two additional C–H bonds and one additional C–C bond compared to the previous alkane, Figure 21.20.

Figure 21.20 Adding a CH_2 unit causes one additional CO_2 molecule and one additional H_2O molecule to be formed on complete combustion. These product molecules are very stable and, therefore, more energy is released when the alkane is burned for every CH_2 unit added.

- When the larger of the two consecutive alkanes undergoes complete combustion, these additional bonds are broken and new bonds are formed. Additional O=O bonds in oxygen must also be broken. As already discussed, breaking bonds is endothermic.
- However, additional C=O bonds in CO_2 and H–O bonds in H_2O are also formed when the larger of the two alkanes burns. As already discussed, making bonds is exothermic.
- In particular, the C=O double bonds formed in the carbon dioxide molecule are very strong. Therefore, the CO_2 molecule is very stable and a lot of energy is released when additional quantities of it are formed.
- In summary, for the additional CH_2 unit in the larger alkane (of two successive alkanes), the energy required for the extra bond breaking upon complete combustion is more than offset by the energy released when making the bonds in the additional CO_2 and H_2O formed.
- If you study the final column in Table 21.7, the increase in energy released on complete combustion is an average of about 650 kJ $mole^{-1}$ for each CH_2 unit added. It is approximately constant for each CH_2 unit added because the same set of bond breaking and bond making energy changes are involved every time.

You will recall that we used alcohol as a fuel in Experiment 21.1. Alcohols also undergo complete combustion to produce carbon dioxide and water. The balanced equations for the complete combustion of the first six primary alcohols are given in Table 21.8

Name of alcohol	Formula	Balanced equation for complete combustion		$\Delta H_{combustion}$
Methanol	CH_3OH	$2CH_3OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 4H_2O_{(l)}$	$\Delta H = -1452$ kJ mol^{-1}	–726 kJ mol^{-1}
Ethanol	C_2H_5OH	$C_2H_5OH_{(l)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(l)}$	$\Delta H = -1367$ kJ mol^{-1}	–1367 kJ mol^{-1}
Propan-1-ol	C_3H_7OH	$2C_3H_7OH_{(l)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 8H_2O_{(l)}$	$\Delta H = -4042$ kJ mol^{-1}	–2021 kJ mol^{-1}
Butan-1-ol	C_4H_9OH	$C_4H_9OH_{(l)} + 6O_{2(g)} \rightarrow 4CO_{2(g)} + 5H_2O_{(l)}$	$\Delta H = -2676$ kJ mol^{-1}	–2676 kJ mol^{-1}
Pentan-1-ol	$C_5H_{11}OH$	$2C_5H_{11}OH_{(l)} + 15O_{2(g)} \rightarrow 10CO_{2(g)} + 12H_2O_{(l)}$	$\Delta H = -6662$ kJ mol^{-1}	–3331 kJ mol^{-1}
Hexan-1-ol	$C_6H_{13}OH$	$C_6H_{13}OH_{(l)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 7H_2O_{(l)}$	$\Delta H = -3984$ kJ mol^{-1}	–3984 kJ mol^{-1}

Table 21.8 Balanced equations and heats of combustion for the complete combustion of primary alcohols up to C6

Note the following from Table 21.8:

- There is a steady increase in the enthalpy of combustion as the number of carbon atoms increases.
- This steady increase is almost linear as shown in Figure 21.19.

The reasons why there is an increase in the enthalpy of combustion every time a CH_2 unit is added are exactly the same in the case of alcohols, as discussed in the case of the alkanes.

If you study Table 21.9, you will notice that the enthalpy of combustion for each alcohol is less than the enthalpy of combustion of the corresponding alkane. You can also see this from studying Figure 21.19. The value of each point on the line representing the alcohols is smaller than the value for the corresponding alkane.

No. of carbons	$\Delta H_{combustion}$ Alkanes	$\Delta H_{combustion}$ Primary alcohols
1	–890 kJ mol^{-1}	–726 kJ mol^{-1}
2	–1560 kJ mol^{-1}	–1367 kJ mol^{-1}
3	–2220 kJ mol^{-1}	–2021 kJ mol^{-1}
4	–2877 kJ mol^{-1}	–2676 kJ mol^{-1}
5	–3535 kJ mol^{-1}	–3331 kJ mol^{-1}
6	–4163 kJ mol^{-1}	–3984 kJ mol^{-1}

Table 21.9 Comparing the enthalpies of combustion of saturated alkanes and primary alcohols up to C6

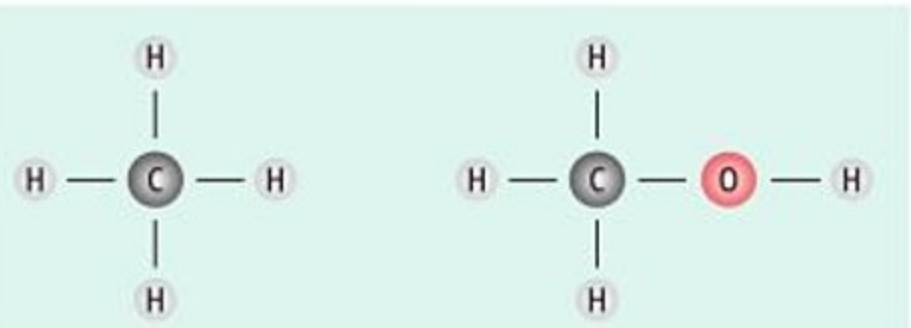


Figure 21.21 Comparing methane and methanol, we see that methanol has an O–H group.

Why do primary alcohols have lower heats of combustion than the corresponding alkanes?

- All alcohols have the –OH functional group. In other words, an oxygen atom is already present in the molecule, Figure 21.21.
- The carbon atom bonded to the –OH group is already partially oxidised.
- Therefore, less energy is released when the primary alcohol is fully oxidised to carbon dioxide and water. In other words, when an alcohol burns, fewer bonds to oxygen need to be formed compared to an alkane of the same number of carbon atoms.
- Recall that according to Hess's Law, the energy released on complete combustion of an alkane to carbon dioxide and water is the sum of the energy released when (i) one oxygen atom is added to convert the alkane to a primary alcohol (ΔH_2 in Figure 21.22) and (ii) the energy released in the complete combustion of that primary alcohol to carbon dioxide and water (ΔH_3 in Figure 21.22).
- Therefore, because alcohols already contain an O atom, they release slightly less energy on combustion than the corresponding alkanes.

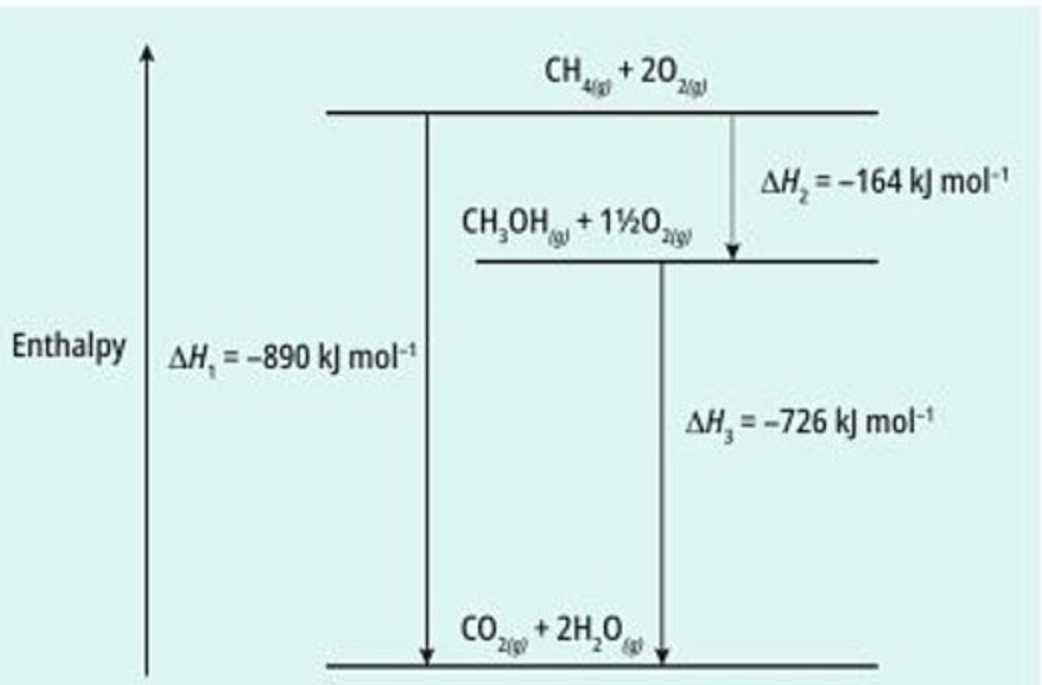


Figure 21.22 Since alcohols already contain an O atom, less energy is released on complete combustion compared to alkanes.

Finally, let's have a quick look at the combustion of alkenes and alkynes. The syllabus specifies that you study compounds with no more than one double or triple bond. Some of these are listed in Tables 21.10 and 21.11.

Combustion of alkenes

Name of hydrocarbon	Formula	Thermochemical equation for complete combustion		$\Delta H_{combustion}$
Ethene	C_2H_4	$C_2H_{4(g)} + 3O_{2(g)} \rightarrow 2CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H = -1411$ kJ mol^{-1}	–1411 kJ mol^{-1}
Propene	C_3H_6	$2C_3H_{6(g)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$	$\Delta H = -4116$ kJ mol^{-1}	–2058 kJ mol^{-1}
But-1-ene	C_4H_8	$C_4H_{8(g)} + 6O_{2(g)} \rightarrow 4CO_{2(g)} + 4H_2O_{(l)}$	$\Delta H = -2710$ kJ mol^{-1}	–2710 kJ mol^{-1}
Pent-1-ene	C_5H_{10}	$2C_5H_{10(g)} + 15O_{2(g)} \rightarrow 10CO_{2(g)} + 10H_2O_{(l)}$	$\Delta H = -6734$ kJ mol^{-1}	–3367 kJ mol^{-1}
Hex-1-ene	C_6H_{12}	$C_6H_{12(g)} + 9O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)}$	$\Delta H = -4023$ kJ mol^{-1}	–4023 kJ mol^{-1}

Table 21.10 Balanced equations and heats of combustion for the complete combustion of alkenes up to C6

Combustion of alkynes

Name of hydrocarbon	Formula	Thermochemical equation for complete combustion		$\Delta H_{combustion}$
Ethyne	C_2H_2	$2C_2H_{2(g)} + 5O_{2(g)} \rightarrow 4CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H = -2600$ kJ mol^{-1}	–1300 kJ mol^{-1}
Propyne	C_3H_4	$C_3H_{4(g)} + 4O_{2(g)} \rightarrow 3CO_{2(g)} + 2H_2O_{(l)}$	$\Delta H = -1866$ kJ mol^{-1}	–1866 kJ mol^{-1}
But-1-yne	C_4H_6	$2C_4H_{6(g)} + 11O_{2(g)} \rightarrow 8CO_{2(g)} + 6H_2O_{(l)}$	$\Delta H = -4870$ kJ mol^{-1}	–2435 kJ mol^{-1}
Pent-1-yne	C_5H_8	$2C_5H_{8(g)} + 13O_{2(g)} \rightarrow 10CO_{2(g)} + 8H_2O_{(l)}$	$\Delta H = -6012$ kJ mol^{-1}	–3006 kJ mol^{-1}
Hex-1-yne	C_6H_{10}	$2C_6H_{10(g)} + 15O_{2(g)} \rightarrow 12CO_{2(g)} + 10H_2O_{(l)}$	$\Delta H = -7156$ kJ mol^{-1}	–3578 kJ mol^{-1}

Table 21.11 Balanced equations for the complete combustion of alkynes up to C6

Let's compare the heats of combustion of alkanes, alkenes and alkynes for compounds of the same number of carbon atoms, Table 21.12.

Number of carbons	$\Delta H_{combustion}$ Alkanes	$\Delta H_{combustion}$ Alkenes	$\Delta H_{combustion}$ Alkynes
1	–890 kJ mol^{-1}	-	-
2	–1560 kJ mol^{-1}	–1411 kJ mol^{-1}	–1300 kJ mol^{-1}
3	–2220 kJ mol^{-1}	–2058 kJ mol^{-1}	–1866 kJ mol^{-1}
4	–2877 kJ mol^{-1}	–2710 kJ mol^{-1}	–2435 kJ mol^{-1}
5	–3510 kJ mol^{-1}	–3367 kJ mol^{-1}	–3006 kJ mol^{-1}
6	–4160 kJ mol^{-1}	–4023 kJ mol^{-1}	–3006 kJ mol^{-1}

Table 21.12 The enthalpies of combustion of alkanes, alkenes and alkynes up to C6

Note in each case that the enthalpy of combustion of each alkene is lower than the corresponding alkane. In other words, less heat is released when the alkene undergoes complete combustion. Also, the enthalpy of combustion of each alkyne is lower than that of an alkene with the same number of carbon atoms. In other words, the quantity of heat released on burning the alkyne is less than is released when an alkene with the same number of carbon atoms undergoes complete combustion. This may also be seen from Figure 21.23.

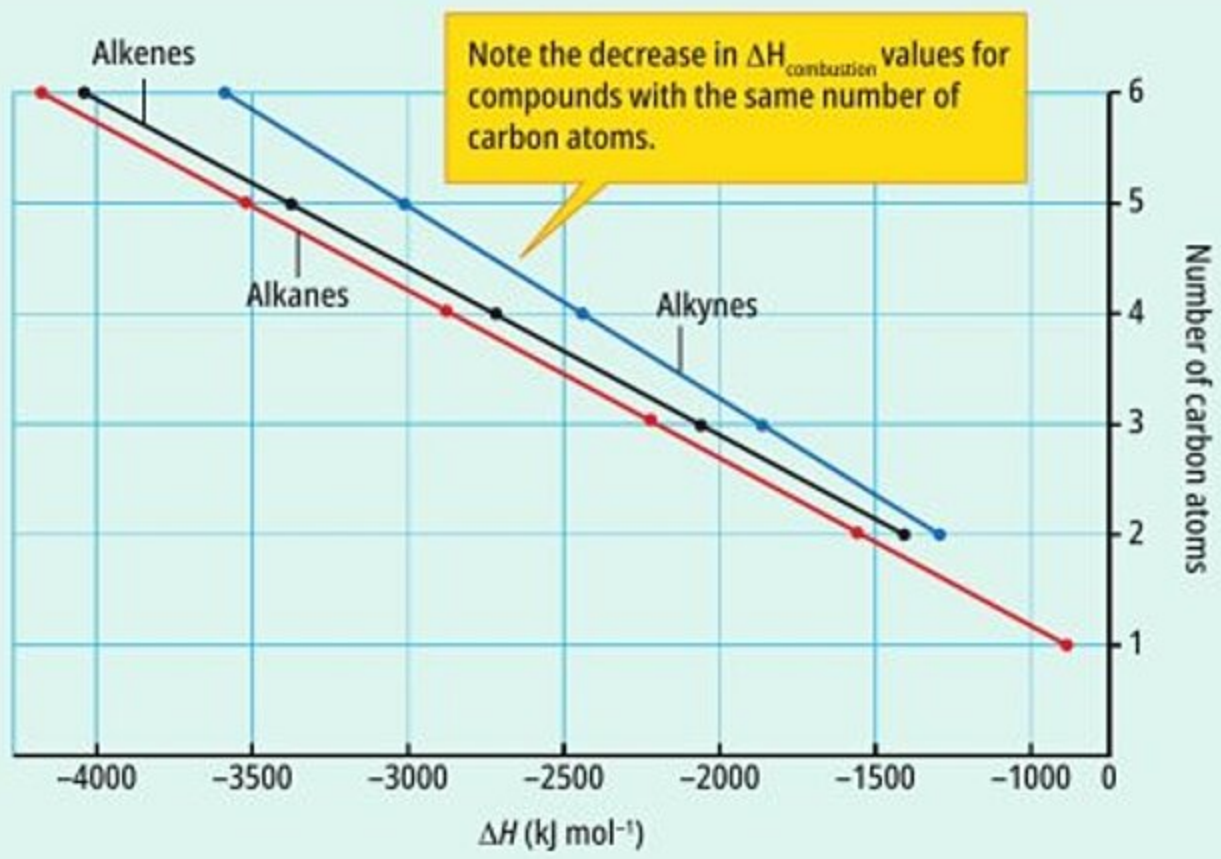


Figure 21.23 Graph of enthalpy of combustion versus number of carbon atoms for some alkanes, alkenes and alkynes up to C6.

Why do alkenes and alkynes have lower heats of combustion than the corresponding alkanes?

The reason for this may be explained as follows:

- There are fewer H atoms in alkenes and alkynes than in alkanes with the same number of carbon atoms, Figure 21.24. This means that alkenes and alkynes form fewer H_2O molecules during combustion. Since the H_2O molecule is quite stable, the reaction to form H_2O is highly exothermic. Forming less H_2O means less energy is released.
- Also in the complete combustion of any of the alkenes or alkynes, a double or triple bond must be broken. Both C=C and C≡C bonds are strong and a lot of energy is required to break them. Therefore, there is less energy released than when an alkane with the same number of carbon atoms is burned.
- Alkynes have the lowest hydrogen content and a very strong C≡C bond. Therefore, an alkyne has the lowest value of heat of combustion compared to the alkane or alkene with the same number of carbon atoms.

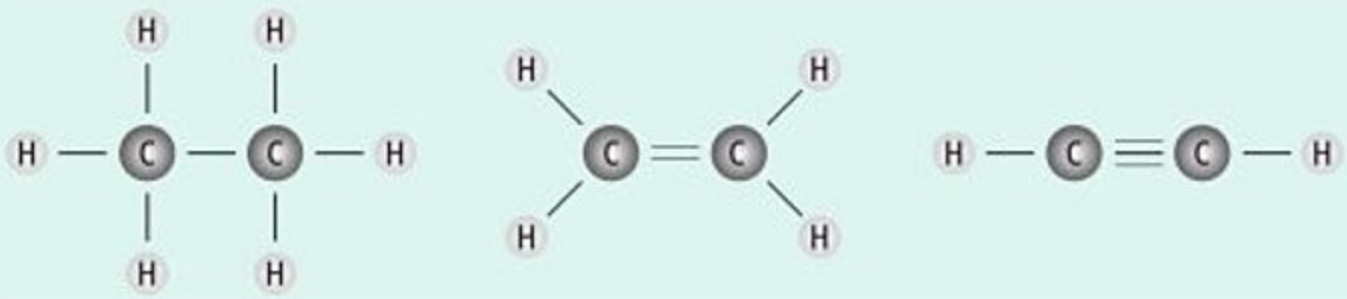


Figure 21.24 Alkenes and alkynes molecules have fewer hydrogen atoms than alkanes with the same number of carbon atoms.

TEST YOURSELF: Attempt Questions 21.6 and W21.23.

Summary What I should know

- Enthalpy of reaction is the heat change when the numbers of moles of reactants indicated in the balanced equation for the reaction react completely.
- The heat of combustion of a substance is the heat change when one mole of the substance is completely burned in excess oxygen.
- Bond enthalpy is the average energy required to break one mole of a particular covalent bond and to separate the neutral atoms completely from each other.
- Enthalpy of neutralisation is the heat change when one mole of H^+ ions from an acid reacts with one mole of OH^- ions from a base.
- The heat of formation of a compound is the heat change that takes place when one mole of a compound is formed from its elements in their standard states.
- Hess's Law states that if a chemical reaction takes place in a number of stages, the total heat change in the separate stages is equal to the heat change if the reaction is carried out in one stage.
- Primary alcohols have lower heats of combustion than the corresponding alkanes.
- Alkenes and alkynes have lower heats of combustion than the corresponding alkanes.

Learning outcomes

At the end of this chapter, I should be able to:			
Explain the concept of enthalpy changes and apply this concept to various types of chemical reactions.	⬡	⬡	⬡
Investigate the heat of combustion of a series of alcohols and the enthalpy of reaction of a neutralisation reaction in the laboratory.	⬡	⬡	⬡
Calculate the enthalpy of a reaction using bond enthalpy values.	⬡	⬡	⬡
Discuss Hess's Law and use it to calculate enthalpies of reactions.	⬡	⬡	⬡
Explain trends in enthalpies of combustion of hydrocarbons and primary alcohols.	⬡	⬡	⬡

Chapter review questions

21.1 **(a)** What name is given to the branch of chemistry that studies heat changes during chemical reactions?

(b) What is the symbol used to represent enthalpy?

(c) Why can the enthalpy of a substance not be measured directly?

(d) What does a negative ΔH value indicate about a chemical reaction?

(e) In a thermochemical equation, explain the term *kJ mol*$^{-1}$.

(f) Give an example of an exothermic reaction from everyday life.

(g) Explain why the physical states of reactants and products must be included in thermochemical equations.

(h) Explain the term *enthalpy of fusion.*

(i) What is the standard temperature at which enthalpy changes are measured?

(j) In the context of thermochemistry, what is meant by the term *surroundings*?

21.2 A group of students performed an experiment to measure the heat of combustion of methanol. They used a copper calorimeter containing 80 cm^3 of water. The initial temperature of the water was 21.0 °C and the final temperature was 63.5 °C. The mass of the spirit burner and methanol before heating was 154.62 g and after heating was 154.01 g. Assuming that all the energy released by the burning alcohol went into heating the water, calculate the heat of combustion of methanol. The specific heat capacity of water is 4200 J kg^{-1} K^{-1}. Density of water is 1 g cm^{-3}.

21.3 Ethene reacts with hydrogen to form ethane as shown in the following equation:

$C_2H_{4(g)} + H_{2(g)} \rightarrow C_2H_{6(g)}$

The standard bond enthalpy values are: C=C double bond = 614 kJ mol^{-1}, H–H = 436 kJ mol^{-1}, C–C = 348 kJ mol^{-1}, C–H = 412 kJ mol^{-1}.

Using these bond enthalpy values, calculate the enthalpy of reaction.

21.4 A student mixed 250 cm^3 of 0.5 M HCl with an equal volume of 0.5 M NaOH in a plastic container. The original temperature of both solutions was 14.8 °C and the final temperature was 18.2 °C. Calculate the enthalpy of neutralisation of hydrochloric acid and sodium hydroxide. Assume that the density of the final solution is 1 g cm^{-3} and its specific heat capacity is 4060 J kg^{-1} K^{-1}.

21.5 Calculate the enthalpy of reaction for the reaction:

$HCOOH_{(l)} \rightarrow CO_{2(g)} + H_2O_{(l)}$

Given the following heats of formation:

$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)}$ $\quad \Delta H = -111$ kJ mol^{-1}

$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(l)}$ $\quad \Delta H = -285.8$ kJ mol^{-1}

$H_{2(g)} + O_{2(g)} + C_{(s)} \rightarrow HCOOH_{(l)}$ $\quad \Delta H = -427.7$ kJ mol^{-1}

21.6 **(a)** Distinguish between complete combustion and incomplete combustion.

(b) What are the only products formed in the complete combustion of hydrocarbons?

(c) Why is carbon monoxide produced in incomplete combustion?

(d) Write the balanced chemical equation for the complete combustion of propane.

(e) Describe and explain the trend in the enthalpy of combustion values for alkanes from methane to hexane

(f) Discuss how the trend in the enthalpy of combustion of primary alcohols compares with the trend in the enthalpy of combustion of alkanes.

(g) Discuss the types of bonds formed in the products of combustion of hydrocarbons and explain their significance in energy release.

22 Electrochemistry

OBJECTIVES

- To give students an understanding of how electricity is produced in galvanic cells and batteries.
- To make students familiar with the system for listing metals in order of their tendency to be oxidised.
- To ensure that students know the chemical reactions that take place in lithium-ion rechargeable batteries and in fuel cells.
- To provide students with the opportunity to investigate the use of electricity to bring about chemical reactions.

22.1 Introduction

The story of the topics in this chapter begins in Bologna, Italy, with an experiment involving a frog's leg! Luigi Galvani was the professor of anatomy in the University of Bologna. In 1771 he noticed something unexpected took place during the dissection of a frog's leg. He observed that if an exposed nerve in the frog's leg was touched by two different metals (e.g. the iron in the scalpel and the copper in a hook), the frog's leg twitched. This surprised him, as the frog was dead! He also observed that the frog's leg also twitched when the brass hook holding the frog came into contact with an iron railing, Figure 22.1.

Figure 22.1 Galvani found that the frog's leg twitched when the nerves in the leg came in contact with two metals.

Galvani thought that the movement of the frog's muscle was due to some sort of 'animal electricity' that came from the frog itself. He wrote up his experiments and sent copies to a friend called Alessandro Volta who worked at the University of Pavia, Italy. Volta realised that what was actually happening was that the electricity was being generated by the two different metals in contact with the liquid material in the frog's leg and this material helped to carry the electric current. In 1800 Volta extended the work of Galvani and constructed a device to produce electricity. This device consisted of round discs of copper and zinc with pieces of cardboard soaked in salt solution between them, Figure 22.2. The discs were piled on top of each other and hence the first battery was called a 'voltaic pile'. It was found that if a wire was attached to the top and bottom of the pile, an electric current flowed. Volta had invented the first battery! You will construct your own voltaic pile in Experiment 22.1 in the Laboratory Notebook accompanying this textbook.

Figure 22.2 Alessandro Volta invented the first battery.

Volta's discovery that chemical reactions involving two different metals and a salt solution generated an electric current is one of the foundation stones of electrochemistry.

Electrochemistry is the branch of chemistry that studies the relationship between chemical reactions and electricity.

Electrochemistry may be divided into two areas:

(i) The use of chemical reactions to produce an electric current (cells or batteries)

(ii) The use of an electric current to bring about chemical reactions (electrolysis).

So let's begin our study of electrochemistry by having a closer look at the use of chemical reactions to produce an electric current.

22.2 Galvanic (Voltaic) cells

We have learned that Volta showed that electricity is produced whenever two different metals are immersed in a conducting solution. We can show this in the laboratory by placing a piece of zinc in a solution of zinc ions and a piece of copper in a solution of copper ions. We link the two solutions using a 'salt bridge', Figure 22.3, and it is observed that a current flows in the connecting wire.

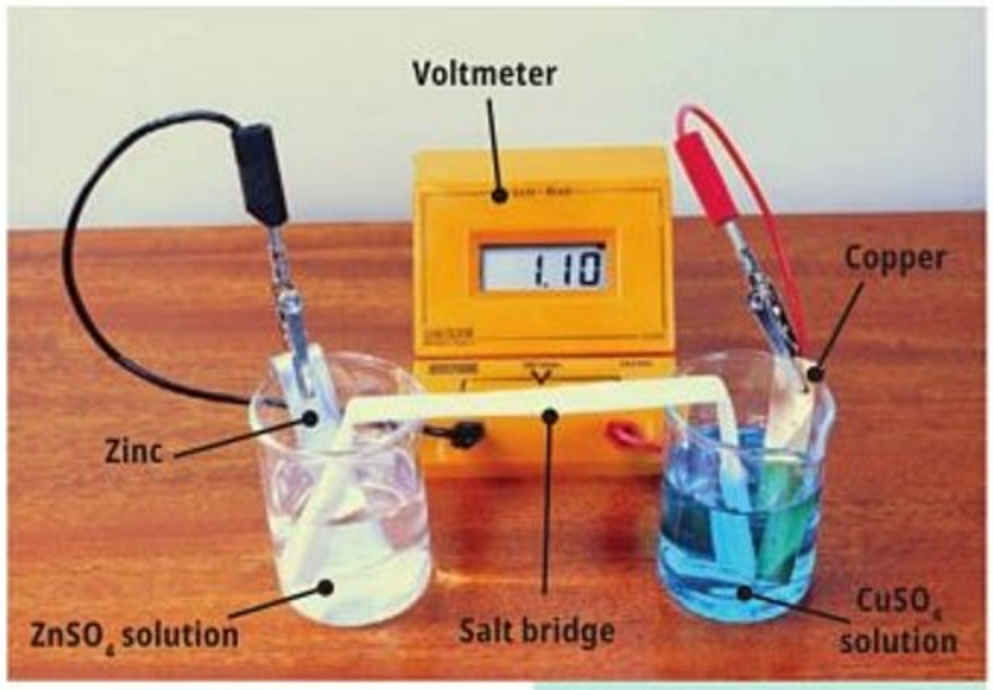


Figure 22.3 This galvanic cell generates a voltage of 1.1 volts.

Note the following terms that are commonly used in electrochemistry:

Electrode: The solid conductor (usually a metal or graphite) that carries the electricity into or out of the cell. In the cell shown in Figure 22.3, the electrodes are the strips of zinc and copper.

Electrolyte: The solution that contains ions and can conduct electricity. In the cell shown in Figure 22.3, the electrolytes are zinc sulfate and copper sulfate.

A cell in which a chemical reaction results in the production of an electric current is called a **galvanic cell** or a **voltaic cell** in honour of Luigi Galvani and Alessandro Volta. In the above cell, a voltage of about 1.1 volts registers on the voltmeter. You may recall from your study of Junior Cycle science that two or more cells connected together is called a battery.

Let's take a closer look at how redox reactions cause an electric current to flow, Figure 22.4.

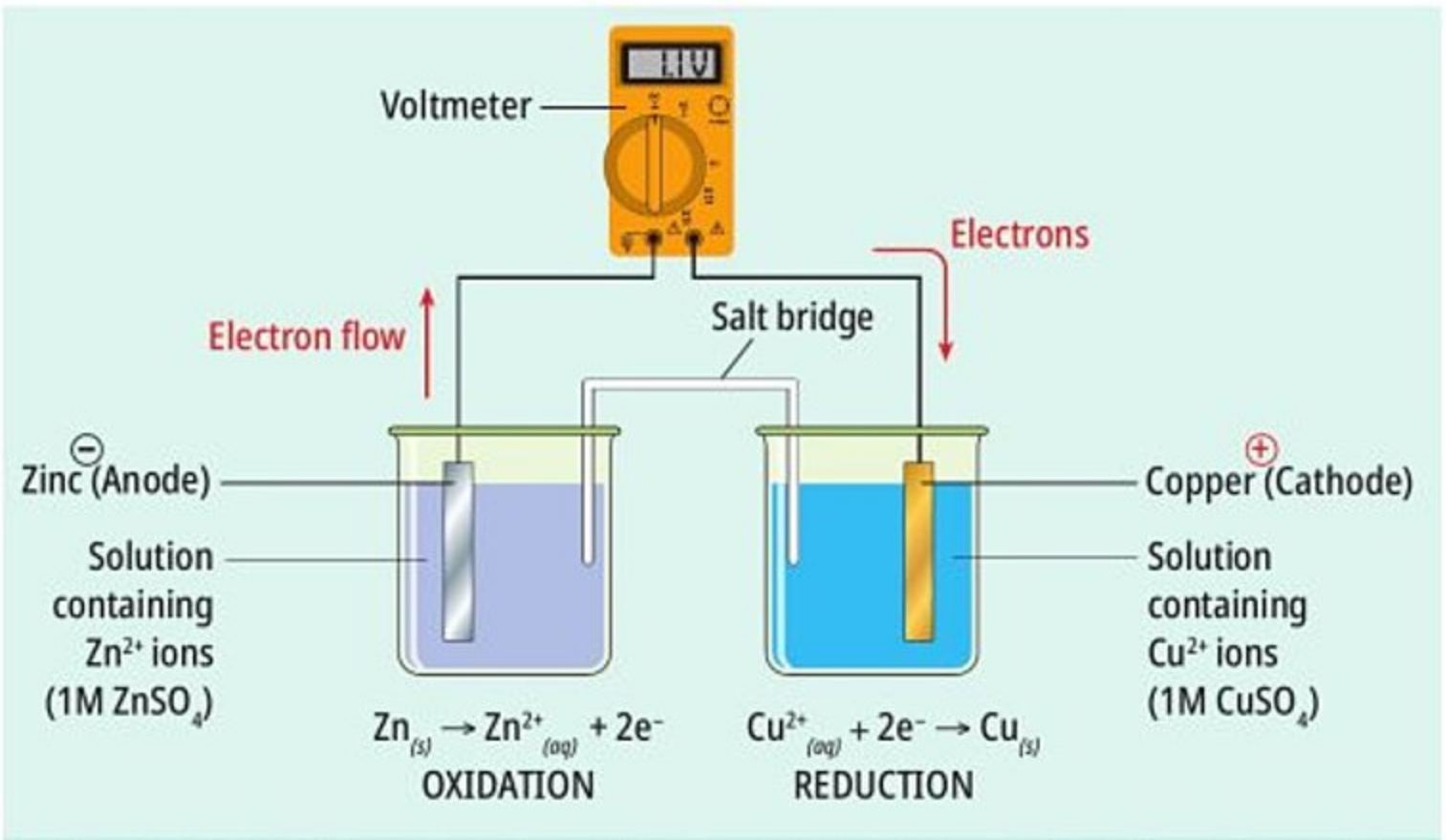


Figure 22.4 Oxidation takes place at the zinc electrode. Reduction takes place at the copper electrode. These redox reactions cause electrons to flow from zinc to copper.

A galvanic cell consists of two half-cells. The current arises because oxidation occurs at one half-cell and reduction occurs at the other half-cell. If you examine Figure 22.4, you will see that each half-cell consists of a metal electrode that is dipping into a solution containing its own metal ions. Also, each half-cell is connected to the other half-cell by a wire and a salt bridge.

Oxidation. At the zinc electrode, zinc atoms lose electrons and form Zn^{2+} ions, i.e. an oxidation reaction takes place:

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$$

These electrons flow through the wire to the copper electrode.

Reduction. At the copper electrode, copper ions accept electrons to become copper atoms, i.e. a reduction reaction takes place to form copper metal:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \downarrow$$

$$\text{Overall reaction : } Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \downarrow$$

- The salt bridge allows ions to flow between the two half-cells without the two solutions mixing directly with each other. It helps to maintain a balance of ions in each part of the cell. The salt bridge could simply consist of a piece of filter paper that has been soaked in a substance such as a solution of potassium chloride or potassium nitrate. Since Zn^{2+} ions build up in the zinc half-cell, then negative ions will move from the salt bridge into the zinc half-cell to maintain balance of ions. Since Cu^{2+} ions are removed from solution in the copper half-cell, positive ions will move from the salt bridge into the copper half-cell to maintain balance of ion.
- The electrode at which **oxidation** occurs is called the **anode**. (Think of the two vowels O and A to help you remember this.) In a galvanic cell, the anode is **negative** and it loses electrons which flow around the wire in the circuit. Think of the electrons going **a**way from the **a**node in a galvanic cell. Zinc is the anode in the galvanic cell shown in Figure 22.4. The phrase 'the anode is eaten away' may help you to remember that when oxidation occurs, the solid zinc metal is converted to Zn^{2+} ions in solution.
- The electrode at which **reduction** occurs is called the **cathode**. In a galvanic cell, the cathode is **positive** and it accepts electrons coming from the anode. Think of electrons **c**oming to the **c**athode. Copper is the cathode in the galvanic cell shown in Figure 22.4. The acronym CROA may also be of help.

We can now define a galvanic cell in terms of oxidation-reduction reactions.

A galvanic (voltaic) cell is a device that converts chemical energy into electrical energy through oxidation-reduction reactions that occur within it.

- Note that a galvanic cell consists of two half-cells.
- A half-cell in electrochemistry is one part of the cell where either oxidation or reduction occurs.
- It typically consists of a metal electrode dipping into a solution containing ions of that metal. (Don't get confused between the cell that you meet in electrochemistry and the cell that you meet when studying biology!)

TEST YOURSELF: Attempt Questions 22.1 and W22.1–W22.2.

22.3 The electrochemical series

We have seen that the voltage generated by the zinc–copper cell is 1.1 volts. If we could assign a particular fraction of this voltage to each individual half-cell, we would then have a measure of the tendency for each of the above two reactions to occur. However, you cannot measure the voltage of a single half-cell because current will only flow when **two** half-cells are connected together. Chemists overcome this problem by choosing a particular half-cell as the standard with which to compare other half-cells. The half-cell chosen as the reference is called the **hydrogen half-cell**. This consists simply of a piece of platinum metal immersed in a 1 M solution of H^+ ions. Hydrogen gas (at atmospheric pressure) is then bubbled over the platinum electrode. A standard half-cell of any other element consists of an electrode of the element immersed in a 1 M solution of its ions.

- Some metals have a greater tendency to lose their outer electrons than other metals, e.g. if zinc is replaced by magnesium in the cell in Figure 22.4, a much higher voltage is observed. This is because magnesium has a far greater tendency to lose electrons than zinc.
- The standard electrode potential value for a metal is the voltage recorded when the standard half-cell of that metal is connected to a standard hydrogen half-cell as shown in Figure 22.5.
- Chemists use the standard **electrode potential of a metal** to describe **the tendency of the metal to lose electrons**, i.e. **the tendency for a metal to be oxidised.**

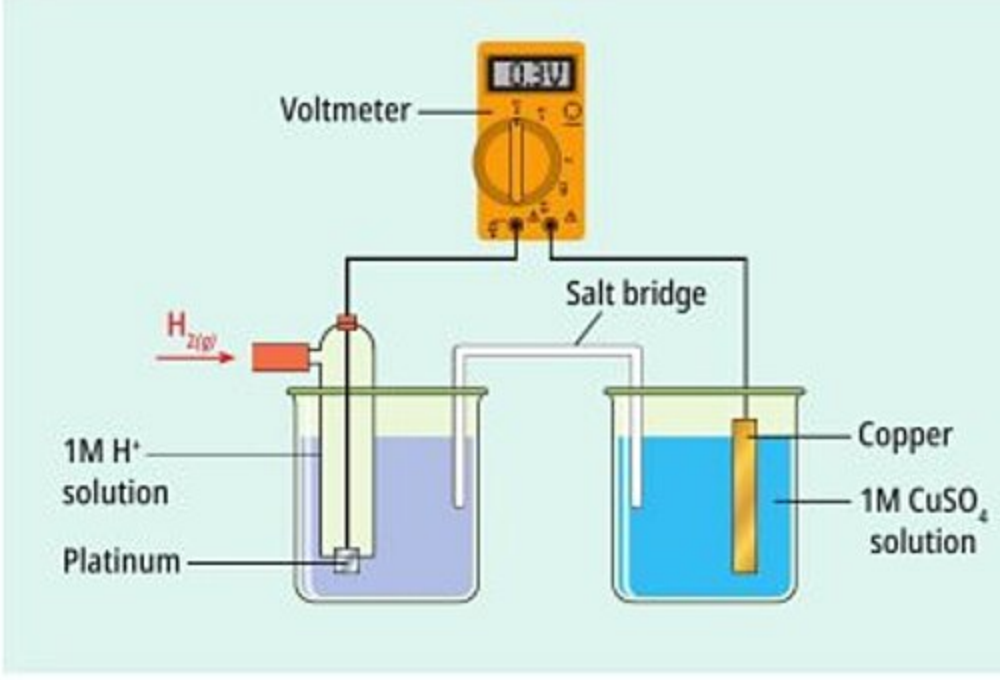


Figure 22.5 The hydrogen half-cell on the left is used to measure the standard electrode potential of copper.

Each element in turn may be connected to the standard hydrogen electrode and the standard electrode potential of the element measured. It is then possible to draw up a table of the elements in order of their standard electrode potentials. Such a table is called the **electrochemical series**.

The **electrochemical series** is a list of elements in order of their standard electrode potentials, i.e. in order of the decreasing tendency for the element to be oxidised (lose electrons) under standard conditions.

Part of the electrochemical series is shown in Table 22.1. You need to know the order of these metals relative to hydrogen. Your teacher will probably award a bar of chocolate to the student in the class who creates the best mnemonic to help remember the order – so get working on this!

The main points about the electrochemical series may be summarised as follows:

- Metals near the top of the table will have a great tendency to lose electrons to form positive ions in solution. Therefore, these metals tend to be very reactive.
- Metals near the bottom of the table have a small tendency to lose electrons and are therefore very unreactive. They may even occur in nature as the pure metal, e.g. gold.
- The electrochemical series is a guide to the relative tendency of metals to lose electrons, i.e. to undergo oxidation.
- The electrochemical series can help predict the likely outcomes of displacement reactions in solution.
- If a length of magnesium ribbon is dipped into a solution of copper ions, the magnesium metal becomes coated with copper, Figure 22.6.

This is because the following reaction occurs:

$$Mg + Cu^{2+} \rightarrow Mg^{2+} + Cu \downarrow$$

Magnesium is above copper in the electrochemical series. Therefore, magnesium has a greater tendency than copper to lose electrons, i.e. the magnesium forces the Cu^{2+} ions to accept electrons. Therefore, the copper is displaced out of solution as copper metal.

- Another example of a displacement reaction occurs when copper metal is added to a solution containing some Ag^{+} ions. Since copper is above silver in the electrochemical series, the copper displaces Ag^{+} ions out of solution as silver metal, Figure 22.7.

The reaction taking place is:

$$Cu + 2Ag^{+} \rightarrow Cu^{2+} + 2Ag \downarrow$$

One example of an application of this displacement reaction in industry is the use of scrap iron to extract copper metal from a solution of copper salts. For example, if scrap iron is added to $CuSO_4$ solution, copper metal is displaced out of solution.

$$Fe + Cu^{2+} \rightarrow Fe^{2+} + Cu \downarrow$$

» Study Example 22.1 in the online resources.

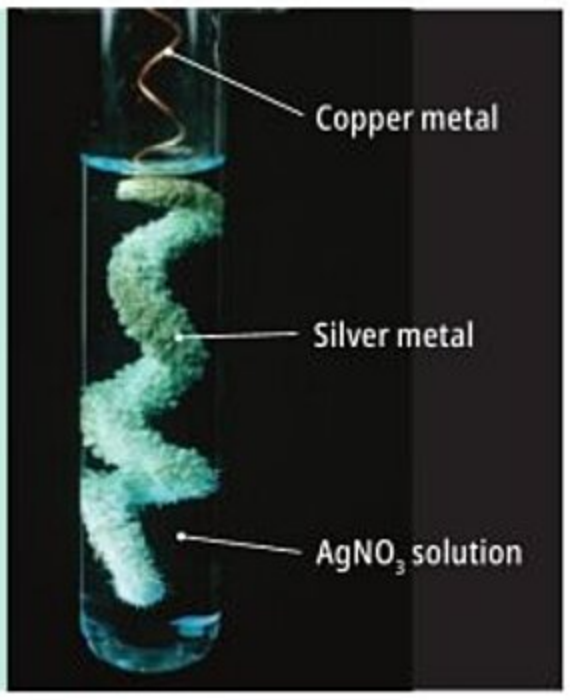
Lithium	Metals near the top of the series have the greatest tendency to lose electrons under standard conditions, i.e. they are easily OXIDISED, forming ions in solution.
Potassium	
Calcium	
Sodium	
Magnesium	
Aluminium	
Zinc	**Becoming less easily oxidised under standard conditions**
Iron	
Lead	
Hydrogen	
Copper	Metals near the bottom of the series tend to be very stable. They have a poor tendency to undergo oxidation (loss of electrons).
Mercury	
Silver	
Gold	

Table 22.1 Part of the electrochemical series

A metal higher up in the electrochemical series will displace another metal that is below it in the electrochemical series from a solution of the ions of that metal.

Figure 22.6 Magnesium is above copper in the electrochemical series. Therefore, magnesium displaces Cu^{2+} ions out of solution as copper metal.

Figure 22.7 This photograph shows what happens when some copper wire is placed in a solution of silver nitrate. Note that the Ag^{+} ions are displaced out of solution as silver metal. Note also that the solution begins to turn blue as Cu^{2+} ions are formed.



The electrochemical series and corrosion

Since metals near the top of the electrochemical series tend to lose electrons readily, these metals are reactive and corrode easily.

Corrosion is any undesired process whereby a metal is converted to one of its compounds.

Metals such as potassium and sodium have to be stored under oil to prevent them reacting with moisture or oxygen in the air. If a piece of potassium or sodium is removed from the jar of oil and sliced in two, a white powder is seen to form quickly on the metal, Figure 22.8. The sodium or potassium forms an oxide of the metal, i.e. it corrodes.

Figure 22.8 Sodium metal is near the top of the electrochemical series. Therefore, it is oxidised quickly when it comes in contact with oxygen in the air.

The most common example of corrosion we see around us is the corrosion of iron and steel. As you are aware, if iron and steel are not treated, they will slowly be converted to rust. Rust is an oxide of iron of formula $Fe_2O_3.xH_2O$. (The amount of water of crystallisation can vary.) Rusting requires the presence of both oxygen and water.

As a general rule, the metals high up in the electrochemical series corrode more quickly than those low down in the series. There are some notable exceptions to this. For example, aluminium is quite high in the electrochemical series but does not appear to corrode. In fact, aluminium does corrode but the oxide of aluminium formed, Al_2O_3, sticks firmly to the metal surface and prevents further corrosion.

There are several ways of preventing corrosion:

1. **Painting and greasing.** Painting is very useful for large structures such as bridges. However, the painting has to be done fairly frequently as corrosion will take place if the metal is scratched. When this happens, the bare metal is then exposed to air and water. For moving parts of machinery, oil and grease are very useful for preventing corrosion.
2. **Galvanising.** In this case, a coating of zinc is used to cover iron or steel to protect the iron or steel from corrosion. Such iron is called **galvanised iron** (named after Galvani). Since zinc is higher than iron in the electrochemical series, it corrodes in preference to the iron, thus protecting the iron. Items such as metal buckets and wheelbarrows are often made from galvanised iron. In addition, galvanised iron is used in building sheds and barns.
3. **Coating of surface with another metal.** In some cases, the iron or steel is coated with a very unreactive metal, e.g. 'tin' cans are made of steel coated with tin. The unreactive tin protects the steel. Chromium is also used as a surface coating, e.g. taps and bathroom fittings all consist of steel coated with chromium to prevent corrosion and also to give a nice shiny finish.
4. **Using sacrificial anodes.** In this method of preventing corrosion, the iron is placed in contact with a metal that is more easily oxidised, e.g. a block of zinc is bolted to iron. In this case, the zinc corrodes rather than the iron, i.e. the zinc is sacrificed to protect the iron. Sometimes, large pieces of zinc are attached to the steel hulls of ships or underground pipes, Figure 22.9. The zinc is oxidised, i.e. the zinc becomes the anode and the anode is eaten away. The zinc needs to be replaced from time to time. The steel of the hull is, therefore, the cathode and cannot corrode. This method of protection is also called **cathodic protection** because the steel is being protected by making it the cathode of the cell.

Figure 22.9 Zinc is bolted onto the steel hull. Since zinc is higher in the electrochemical series, it corrodes in preference to the steel hull. Zinc is the sacrificial anode.

TEST YOURSELF: Attempt Questions 22.2–22.3 and W22.3.

22.4 Primary (non-rechargeable) and secondary (rechargeable) cells

As already discussed, a galvanic cell produces a flow of electrons as a result of chemical reactions taking place at the anode and cathode. You may recall from your study of electricity in Junior Cycle science that **a battery is a collection of two or more cells connected together**. For example, when four 1.5 volt zinc-carbon cells are connected in series, the total voltage is 6 V, Figure 22.10. (Connecting the cells in series means that the positive end of one cell is connected to the negative end of another cell.)

In everyday speech we often use the terms *cell* and *battery* to mean the same thing, but you need to be clear on the difference. Each of the units shown in Figure 22.10 is a cell and it is only when the cells are connected together that we have a battery.

So called 'zinc-carbon' cells and 'alkaline' cells are types of cells commonly used in items such as remote-control devices, flashlights and wall clocks. These cells are examples of primary cells because they are non-rechargeable.

Figure 22.10 Each of the cells shown has a voltage of 1.5 V. When the four cells are connected in series, the total voltage is 4 x 1.5 V = 6 V.

A **primary cell** is a type of galvanic cell that is designed for single use only. When the chemical reactions that take place inside a primary cell have been completed, the cell cannot be recharged as the chemical reactions are irreversible.

As you are aware, the battery in your mobile phone can be recharged, Figure 22.11. A typical smartphone contains one 'lithium-ion' cell. Since lithium-ion cells can be recharged, they are classified as secondary cells.

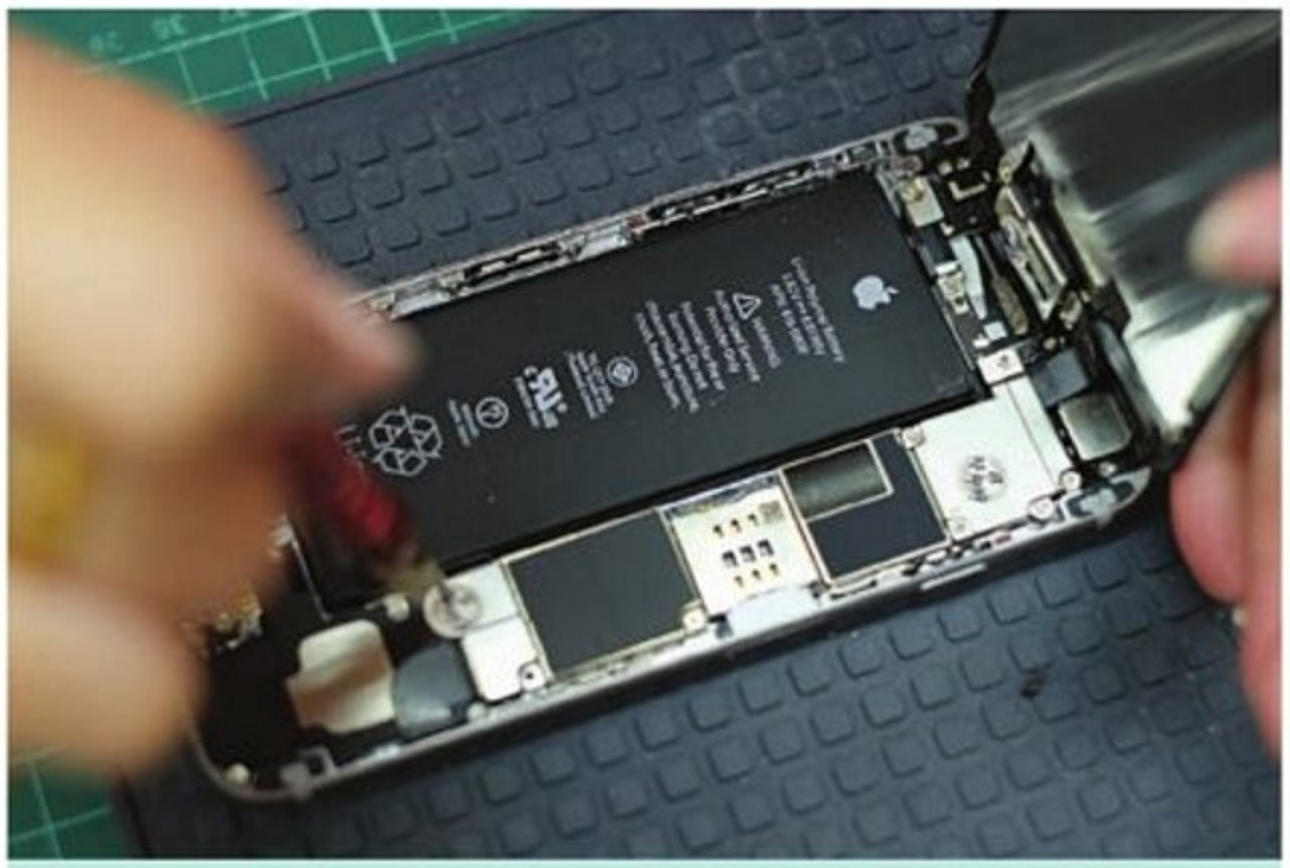


Figure 22.11 Lithium-ion cells are classified as secondary cells since they can be recharged.

A **secondary cell** is a type of galvanic cell that can be recharged. The chemical reactions that take place inside the cell are reversible. Therefore, the cell can be reused many times.

A lithium-ion cell has a voltage of about 3.8 volts. Smartphones usually contain just one lithium-ion cell since a voltage of about 3.8 V is sufficient to power the electronics in the smartphone. The use of a single cell also reduces the size and mass of the smartphone. The invention and development of lithium-ion batteries has revolutionised the world of electronics, Figure 22.12.

Figure 22.12

John Goodenough (1922–2023)
Stanley Whittingham (1941–)
Akira Yoshino (1948–)

The Nobel Prize in chemistry was awarded in 2019 to John Goodenough, Stanley Whittingham and Akira Yoshino for their work in developing the lithium-ion battery. The Nobel citation stated that 'this rechargeable battery laid the foundation of wireless electronics such as mobile phones and laptops. It also makes a fossil fuel-free world possible, as it is used for everything from powering electric cars to storing energy from renewable sources.'

Another example of a secondary cell is the lead-acid battery used in cars. This consists of six 2 V cells in series and has a voltage of about 12 volts.

A comparison between primary and secondary cells is summarised in Table 22.2.

Feature	Primary cell	Secondary cell
Rechargeable	No	Yes
Chemical reactions	Not reversible	Reversible
Usage	Single use only	Can be reused many times
Voltage of one cell	1.5 V (approx.) depending on type of cell	3.8 V (approx.) for lithium-ion cell; 2V for lead-acid
Environmental impact	Higher impact on environment	Lower impact since can be reused
Example	Zinc-carbon, alkaline, lithium	Lithium-ion, lead-acid

Table 22.2 Comparing a primary cell and a secondary cell

Note in Table 22.2 that non-rechargeable batteries also include lithium batteries. These contain lithium metal or lithium compounds and are commonly found in watches, cameras and calculators. We will not be studying these in this course, as rechargeable lithium-ion cells are far more important.

Let's now take a closer look at a lithium-ion cell. To understand how a lithium-ion cell works, we first discuss what happens when the lithium-ion cell is being used to power a device. Then we will look at what happens when a lithium-ion cell is being recharged.

The lithium-ion cell when being used to supply electricity to power a device (discharging)

We will tell the story in a number of stages and let's assume we are describing the lithium-ion cell in a mobile phone.

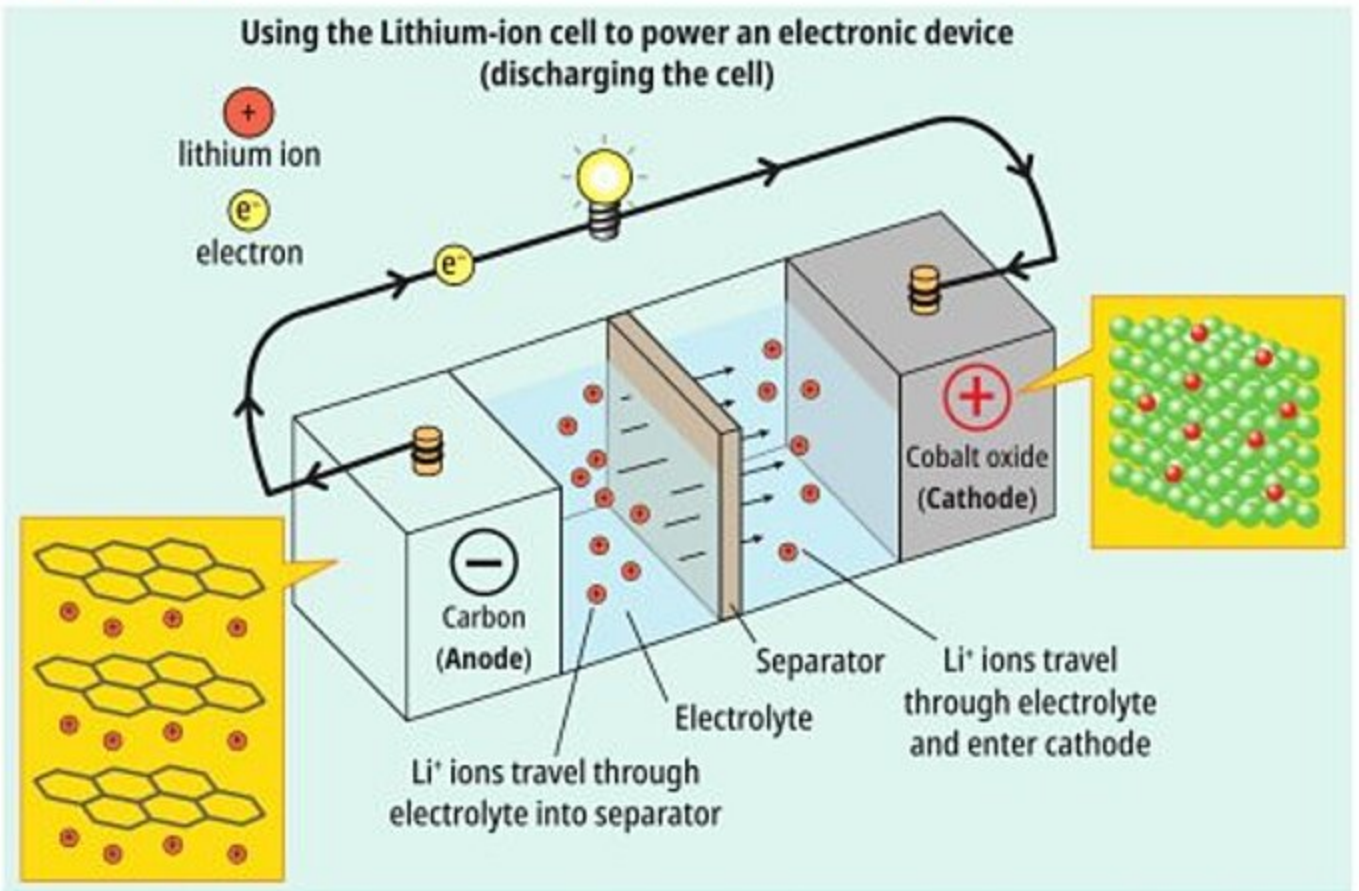


Figure 22.13 Diagram of lithium-ion cell when current is being drawn from it to operate an electronic device

Stage 1: The parts of the cell

If you study the diagram in Figure 22.13, you will see that there are two electrodes in the lithium-ion cell.

The carbon electrode

- The electrode on the left is made of carbon in the form of **graphite**. Graphite is an allotrope of carbon and will be discussed in more detail in Chapter 23. The carbon electrode is the negative electrode (anode) during discharge of the cell.
- Graphite consists of flat layers of carbon atoms arranged in hexagons (Chapter 23). Before the mobile phone is switched on, layers of lithium ions are inserted in between these layers. The layered structure of graphite is perfect for hosting the lithium ions. The technical term used to describe the hosting of the lithium ions is **intercalation**. This word was originally used for inserting extra days into a calendar. In chemistry it is used to describe inserting lithium ions between layers of particles such as atoms.

The cobalt oxide electrode

- The electrode on the right is made of a substance called cobalt oxide, CoO_2. This is the positive electrode (cathode) during discharge of the cell.

The electrolyte

- This is a liquid or gel solution. It consists of lithium salts dissolved in an organic solvent. An organic solvent has to be used as lithium reacts with water.
- The electrolyte allows Li^+ ions to pass through but does not allow electrons to pass through it.
- The electrolyte is in contact with both the anode and the cathode to ensure that Li^+ ions can move in both directions between the anode and the cathode.

The separator (barrier)

- It is a thin plastic film. It may also be called the barrier.
- It allows Li^+ ions to pass through it in both directions.
- It prevents electrons from flowing directly between the electrodes. This would short circuit the cell.

Stage 2: Reaction at carbon electrode: electron flow

- When the mobile phone is switched on, the carbon electrode is connected to the cobalt oxide electrode via the external circuit.
- The following spontaneous oxidation reaction occurs at the anode:

Reaction at carbon electrode (anode):

$LiC_6 \rightarrow Li^+ + e^- + C_6$

The reaction is spontaneous because lithium, being at the top of the electrochemical series, has a strong tendency to lose electrons. Recall, that lithium is so reactive that it must be stored under oil to prevent it coming in contact with the oxygen in the air, Figure 22.14.

Figure 22.14 Lithium, similar to sodium and potassium, is so reactive that it has to be stored under oil, to prevent it spontaneously reacting with the oxygen in the air.

LiC_6 is not a chemical compound but a formula indicating that for every six carbon atoms in the graphite structure, there is one lithium ion between the layers of carbon atoms. Think of the layers of carbon atoms like individual pages stacked vertically with lithium ions between the pages. When the lithium is stored within the graphite in this form, it is very stable.

- The electrons that are released in the above reaction flow from the carbon electrode of the cell into the external circuit of the mobile phone and then to the cobalt oxide electrode. Note in Figure 22.13 that the direction of flow of electrons is from the carbon electrode (negative) to the part of the mobile phone that require energy and then to the cobalt oxide (positive) electrode.

Stage 3: Lithium-ion flow

- We have seen in stage 2 that the electrons leave the carbon anode and travel to the cobalt oxide cathode through the external circuit. It is clear from the equation for the reaction that takes place at the carbon anode, for each electron that leaves the carbon anode, a Li^+ ion is left behind.
- As you continue to use your mobile phone, Li^+ ions are building up at the carbon anode.
- Negative charge is building up at the cobalt oxide cathode.
- If the Li^+ ions did not move, the flow of electrons would stop due to this charge imbalance.
- Therefore, to balance the charge and keep the battery electrically neutral overall, Li^+ ions move from the carbon through the electrolyte and separator to the cobalt oxide cathode.

Note the difference between electron flow and lithium-ion flow. Electrons flow through the external circuit and Li^+ ions flow though the internal electrolyte.

Stage 4: Reaction at cobalt oxide electrode

- At the cathode, the electrons that arrive via the external circuit combine with the Li^+ ions that arrive via the internal electrolyte. This may be written as:

Reaction at cobalt oxide electrode (cathode):

$$Li^+ + e^- + CoO_2 \longrightarrow \underset{\text{Lithium cobalt oxide}}{LiCoO_2}$$

- This reduction reaction (Co^{4+} in CoO_2 to Co^{3+} in $LiCoO_2$) is important as it allows the lithium ions to be held in the crystal lattice of lithium cobalt oxide. Similar to the way that lithium ions were stored in the carbon electrode (anode), lithium ions are also stored in the cobalt oxide (cathode).
- Chemists have discovered that the Li^+ ions are small enough to fit in (intercalate) between the gaps of the much larger cobalt ions in the crystal lattice of lithium cobalt oxide. The Li^+ ions are only inserted into the gaps. They do not form strong bonds – this is important when we need to reverse the reaction in the process of recharging the battery.

Stage 5: The overall process involved in discharging the lithium-ion cell

We can summarise the above two reactions as follows:

Reaction at carbon anode: $LiC_6 \rightarrow Li^+ + e^- + C_6$

Reaction at cobalt oxide cathode:

$Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$

Overall: $LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$

This equation tells us that the overall result is the transfer of lithium ions from the carbon electrode to the cobalt oxide electrode. This transfer releases electrical energy to power the device. When the above reaction stops, there is no longer any source of power for the mobile phone and the cell needs to be recharged. If you understand the above stages, then understanding the recharging process is a piece of cake, since it is just the reverse of everything above!

The lithium-ion cell when being recharged

When the lithium-ion cell is being recharged, an external power source (the charger) forces electrons in the opposite direction, Figure 22.15. Note that electrons are now entering the carbon electrode. This causes the redox reactions at the carbon electrode and the cobalt oxide electrode to be reversed.

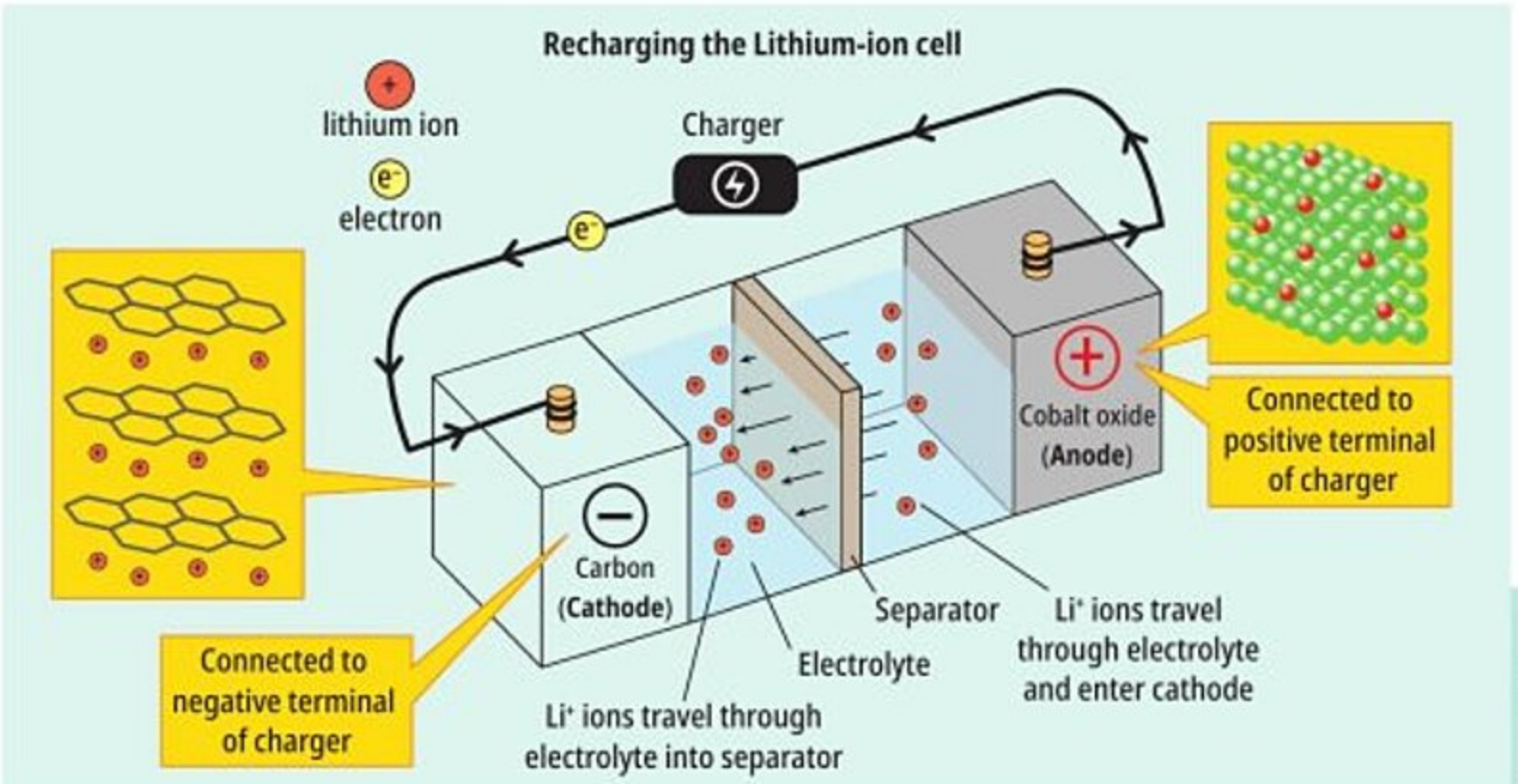


Figure 22.15 This diagram shows a lithium-ion cell when it is being recharged.

- Electrons from the charger cause the reaction at the electrodes to be reversed:

Reaction at cobalt oxide electrode: $LiCoO_2 \rightarrow Li^+ + e^- + CoO_2$

Reaction at carbon electrode: $Li^+ + e^- + C_6 \rightarrow LiC_6$

Overall: $C_6 + LiCoO_2 \rightarrow LiC_6 + CoO_2$

A summary of the discharging and charging of a lithium-ion cell is given in Table 22.3

Feature	Discharging (cell is supplying power to a device)	Charging (energy from an external source is used to store power in the cell)
Electron flow	Carbon electrode → external circuit → cobalt oxide electrode	Cobalt oxide electrode → external circuit → carbon electrode
Li^+ flow	Carbon electrode → electrolyte → cobalt oxide electrode	Cobalt oxide electrode → electrolyte → carbon electrode
Reaction at carbon electrode	$LiC_6 \rightarrow Li^+ + e^- + C_6$ Oxidation (Anode)	$Li^+ + e^- + C_6 \rightarrow LiC_6$ Reduction (Cathode)
Reaction at cobalt oxide electrode	$Li^+ + e^- + CoO_2 \rightarrow LiCoO_2$ Reduction (Cathode)	$LiCoO_2 \rightarrow Li^+ + e^- + CoO_2$ Oxidation (Anode)
Overall reaction	$LiC_6 + CoO_2 \rightarrow C_6 + LiCoO_2$	$C_6 + LiCoO_2 \rightarrow LiC_6 + CoO_2$
Type of reaction	Redox reactions are spontaneous. Galvanic cell.	External energy is used to force the reactions to take place in the opposite direction. Electrolysis of $LiCoO_2$. Electrolytic cell.

Table 22.3 Summary of the discharging and charging of a lithium-ion cell

The cell is often called a 'rocking chair' cell as the lithium rocks between the carbon electrode and the cobalt oxide electrode.

As we come near the end of our story about the lithium-ion cell, make sure that you can summarise the function of the following three components:

Functions of carbon electrode

- Enables oxidation to take place when cell is in use to power devices.
- Releases lithium ions and electrons when cell is in use to power devices.
- Enables reduction to take place when cell is being recharged.
- Stores lithium ions when the cell is charged.

Functions of cobalt oxide electrode

- Enables reduction to take place when cell is in use to power devices.
- Receives electrons and lithium ions when cell is in use to power devices.
- Enables oxidation to take place when cell is being recharged.
- Stores lithium ions when cell is in use to power devices.

Functions of electrolyte

- Allows movement of lithium ions from anode to cathode and cathode to anode.
- Does not allow movement of electrons through it. Electrons must move in external circuit to power the device.
- We now discuss briefly the life cycle of a lithium-ion cell.

The life cycle of a lithium-ion cell

Mining

- In some countries such as Chile, Argentina and Bolivia, lithium is extracted from salty liquids (called brines) found underground or near the Earth's surface. The salty liquid is pumped from the ground and poured into large pools to allow the water to evaporate, Figure 22.16. After the precipitation of other salts, the liquid that remains consists of about 25% lithium chloride.
- In Australia a lithium-containing mineral called spodumene is blasted out of open pits. Most of this is sent to China where the lithium metal is extracted.
- Since extraction from brines uses energy from the Sun, it is a more sustainable method than rock mining, which requires a lot of heavy machinery for crushing and transporting the rocks containing the lithium.

Figure 22.16 This photo shows large pool of salty liquids called brines in the Atacama Desert, Chile. The water is allowed to evaporate leaving behind salts from which lithium and other metals can be extracted.

Usage and applications

Some uses and applications of lithium-ion batteries are summarised in Figure 22.17.

1. Consumer electronics: phones, laptops, tablets

2. Electric vehicles: cars, scooters, e-bikes

3. Energy storage: home battery systems from solar cells on roof

4. Tools: cordless power tools

5. Backup power: power banks (portable phone chargers)

Figure 22.17 Some uses and applications of lithium-ion batteries

Disposal of lithium-ion batteries

One of the major problems with improper disposal of lithium-ion batteries is the fire hazard associated with this type of battery, Figure 22.18.

Fires can be caused by physical damage to the battery. If the battery is crushed or punctured, it is possible that the separator between the electrodes will be damaged. This can cause an internal short circuit, and the heat generated can cause a fire. The battery is flammable because of the organic solvents in the electrolyte. Also, if the battery is damaged, it is possible that the lithium may react with water to release flammable hydrogen gas.

Other problems caused by the improper disposal of lithium-ion batteries are the leaching of metals such as cobalt and copper into the soil and waterways.

Figure 22.18 This fire was caused by a damaged lithium-ion battery in the laptop.

Recycling of lithium-ion batteries

Recycling of lithium-ion batteries is quite complex and expensive. Lithium-ion batteries contain the metals lithium, cobalt and copper. In addition, they contain carbon, plastic separators and flammable organic electrolytes.

Batteries are often glued or sealed into items such as mobile phones and laptops. This means that disassembling them by hand can be slow and dangerous. It is estimated by some researchers that only 5% to 10% of lithium-ion batteries are properly recycled worldwide. A lot of research is currently being undertaken to develop new systems to extract the metals from lithium-ion batteries. In addition, manufacturers are being encouraged to design lithium-ion batteries that are easier to disassemble.

TEST YOURSELF: Attempt Questions 22.4 and W22.4.

22.1 Experiment

Full details of these experiments are given in Experiment No. 21 in the Laboratory Notebook accompanying this textbook.

Student Experiment No. 21

Experiment 22.1A To construct a galvanic cell and investigate its operation

Experiment 22.1B To construct a Voltaic pile and investigate its operation

Experiment 22.1C To investigate displacement reactions of some metals from solutions of their salts

22.5 Fuel cells

In recent years a lot of research is being undertaken to move away from depending on the burning of fossil fuels to generate electricity or as fuels in our cars. One area in which this research is taking place is in the development of fuel cells. A fuel cell is a very efficient type of galvanic cell.

A **fuel cell** is a device that converts the chemical energy stored in a fuel directly into electrical energy. A fuel cell needs a continuous supply of chemicals.

There is no combustion involved in a fuel cell. Fuel cells work by using oxidation-reduction reactions to produce electricity.

To explain the operation of a fuel cell, let's consider the hydrogen fuel cell, Figure 22.19.

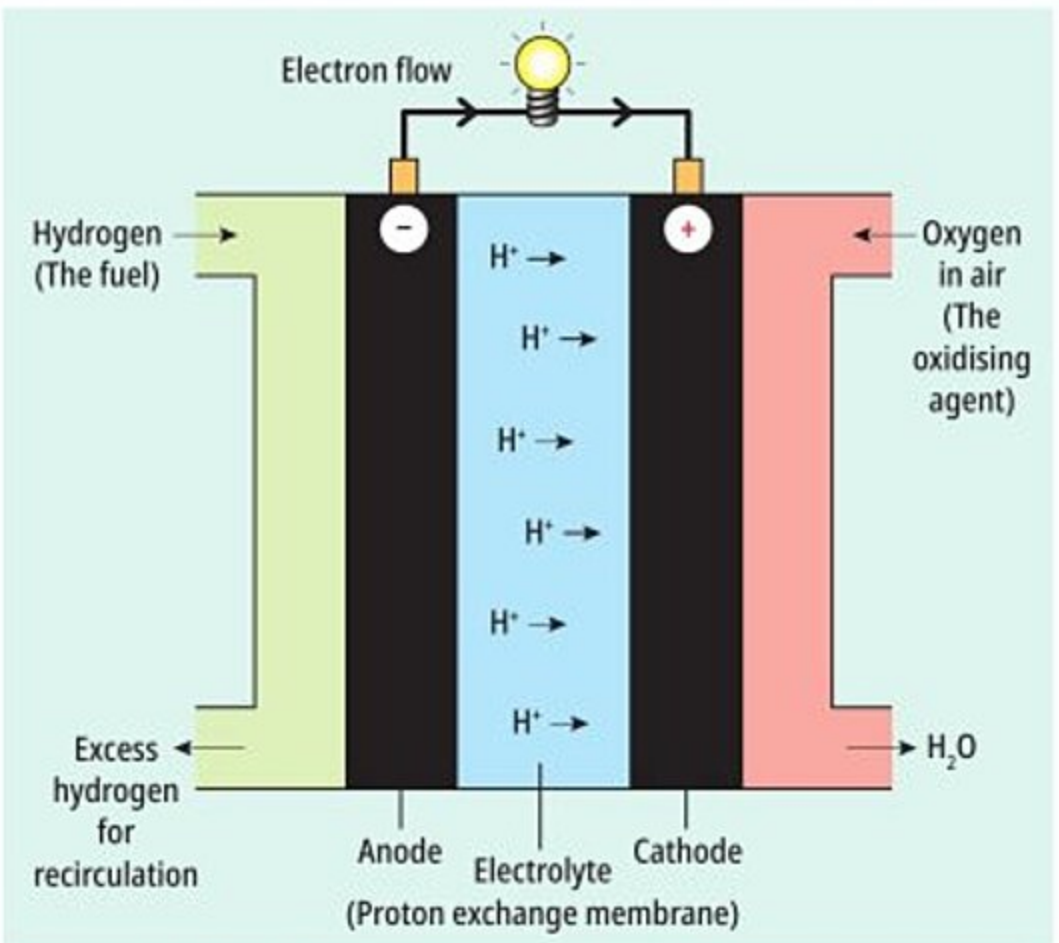


Figure 22.19 A hydrogen-oxygen fuel cell

Unlike batteries which are stores of energy, fuel cells can generate electricity (energy) continuously as long as the fuel and an oxidising agent are supplied.

The main points about the hydrogen-oxygen fuel cell may be explained as follows:

Step 1: Hydrogen gas at the negative electrode

- The fuel is hydrogen and the oxidising agent is oxygen – usually oxygen from the air.
- Hydrogen gas (H_2) is fed to the **negative** electrode (**anode**).
- The anode is made of porous carbon containing a platinum catalyst.
- The porous carbon helps the gas to flow through it.
- The platinum catalyst helps the following **oxidation** reaction to take place:

Reaction at negative electrode:

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^-$$

- Carbon conducts electricity. Therefore, the electrons produced at the anode, can flow through an external circuit to the cathode (positive electrode).
- The function of the anode is to provide a site for the above oxidation reaction to take place.

Step 2: Movement of H^+ ions through the electrolyte

- The H^+ ions produced at the negative electrode travel through an electrolyte to the positive electrode.
- The electrolyte is a solid plastic membrane – it looks like a small plastic sheet. It is of a special type of plastic which allows H^+ ions to pass through it as the ions travel from the negative electrode to the positive electrode.
- The electrolyte is commonly called a **proton exchange membrane**.
- The membrane blocks electrons from passing through it. This forces the electrons to flow in the external circuit.
- The membrane also prevents the hydrogen and oxygen from mixing.
- The membrane has to be kept moist to allow the H^+ ions to pass through it.
- Note that the electrolyte has three functions:

(i) to allow H^+ ions to pass through it.

(ii) to prevent electrons from passing through it.

(iii) to prevent the hydrogen and oxygen from mixing.

Step 3: Oxygen gas at the positive electrode

- Oxygen gas is fed in at the positive electrode (cathode). The oxygen is supplied in air rather than as pure O_2.
- The cathode is made from a similar material to the anode, i.e. porous carbon containing a platinum catalyst.
- The H^+ ions that have travelled from the anode through the membrane react with the oxygen gas and electrons from the external circuit to make water.
  The platinum catalyst helps to improve the efficiency of this reaction.

  The **reduction** reaction that takes place at the **positive** electrode **(cathode)** may be summarised as follows:
- **Reaction at positive electrode:** $\frac{1}{2}O_{2(g)} + 2H^+_{(aq)} + 2e^- \rightarrow H_2O_{(l)}$
- **Overall reaction:** $H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)}$
- Note that in the overall reaction, water is the only product, i.e. zero carbon emissions.

Other fuel cells that use methanol and methane as fuels instead of hydrogen also exist. However, these need not concern us in this course.

Fuel cells and transport

A photograph of a fuel cell in a hydrogen-powered car is shown in Figure 22.20. A single hydrogen-oxygen fuel cell produces a voltage of only about 0.7 V. Therefore, in a typical car there are about 300–400 of these fuel cells connected together.

The car contains a high-pressure hydrogen tank. Hydrogen gas is fed into the negative side of the stack of fuel cells. Oxygen is supplied by air that is drawn in through vents. The electricity is generated as described above and is used to power the electric motor that turns the wheels of the car. Hydrogen-powered cars move smoothly and quietly – similar to electric cars. While electric cars require batteries to be recharged, the tanks in cars with fuel cells need to be refilled with hydrogen gas.

Figure 22.20 This car contains a fuel cell that is powered by hydrogen gas. The fuel cell provides the electricity to power the motor that turns the wheels of the car.

In Table 22.4 we compare a chemical cell with a fuel cell. Study this table carefully, as comparing a chemical cell with a fuel cell is one of the learning outcomes listed on the syllabus.

Feature	Chemical cell	Fuel cell
1. **Source of energy**	Reactants are stored inside the cell.	The fuel and oxidising agent are continuously fed into the cell.
2. **Supply of reactants**	Once all the reactants have been used up, the cell no longer works.	No limit to supply of reactants as the fuel and oxidising agent are continuously supplied.
3. **Charging**	Primary cells cannot be recharged. Secondary cells can be recharged.	No need for recharging as the fuel is continuously supplied.
4. **Environmental impact**	Environmental impact can be high due to extraction of metals (mining) and disposal problems.	Water is the only product in hydrogen fuel cells. Environmental impact low – especially if using 'green hydrogen'.

Table 22.4 Comparing a chemical cell with a fuel cell

Note that the same type of energy conversion takes place in both a chemical cell and a fuel cell, i.e. chemical energy is converted to electrical energy using redox reactions.

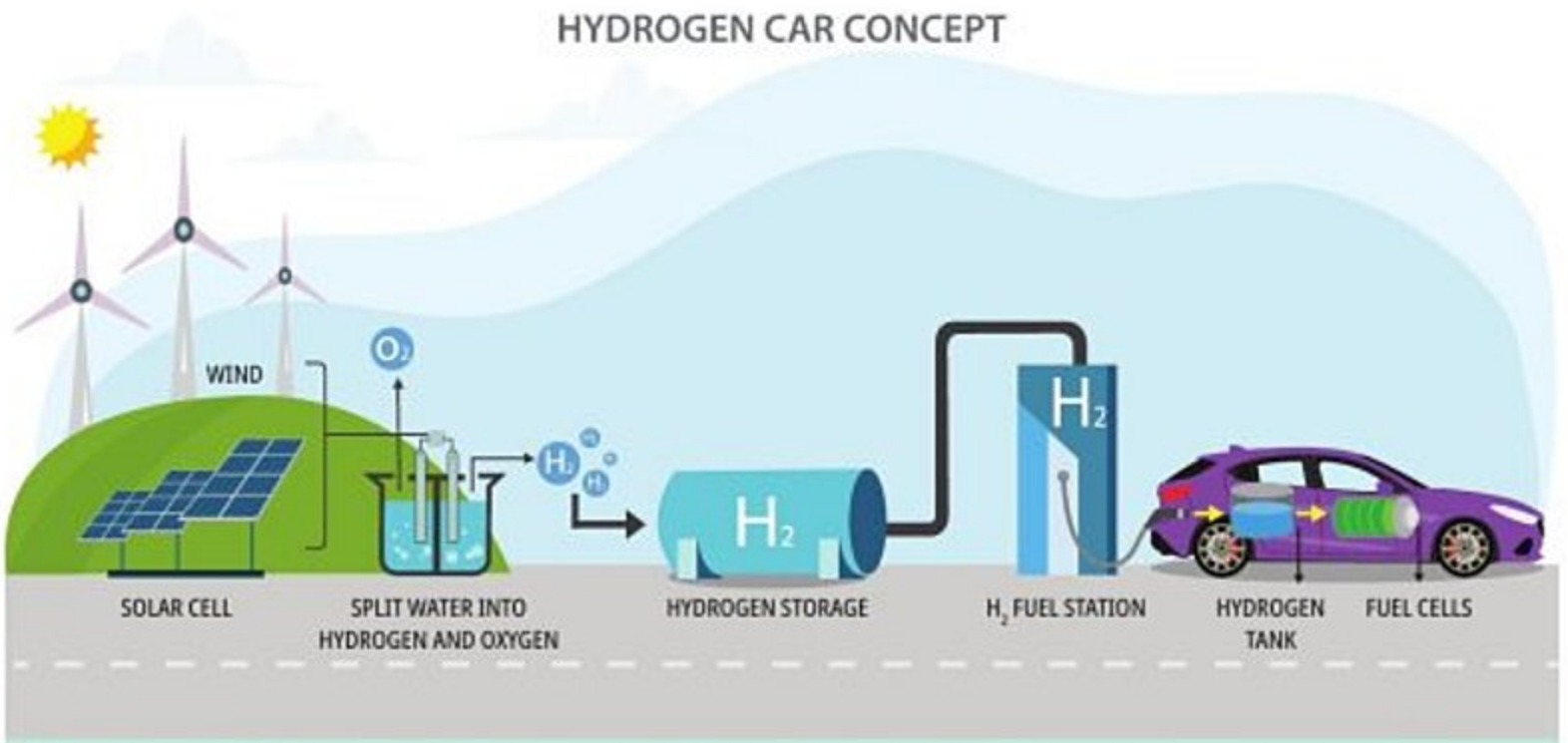


Figure 22.21 Green hydrogen is hydrogen that is produced by splitting water into hydrogen and oxygen using electricity from wind or solar energy.

You may have heard the term *green hydrogen* being used when speaking about the use of hydrogen as a fuel, Figure 22.21. Hydrogen is a colourless gas but the 'green' refers to hydrogen gas that has been manufactured by splitting water into hydrogen and oxygen using electricity that has been generated from wind or solar energy. (We will be studying how water is split into hydrogen and oxygen in the next section.) This manufacturing process does not release any carbon dioxide and hence does not damage the environment. Hydrogen may also be produced industrially by burning fossil fuels but hydrogen from this source would not be classified as green hydrogen.

The principle of a car being powered by fuel-cell technology may be demonstrated by means of a toy car, Figure 22.22. Firstly, hydrogen and oxygen gases are generated by splitting the water into these two gases. The two gases are stored in small onboard tanks. Once sufficient gases are collected, the hydrogen fuel cell powers the electric motor of the toy car – and off it goes!

There are still some challenges in using hydrogen as a fuel. For example, hydrogen is a flammable gas and forms an explosive mixture with air. It has to be stored under high pressure. In Ireland there is still no infrastructure in the support of refuelling stations, to support hydrogen car private ownership. Furthermore, green hydrogen is not readily available and producing hydrogen from fossil fuels is not desirable. However, technology associated with hydrogen as a fuel is improving rapidly and, without doubt, some of you reading this will have your own hydrogen-powered car some day!

TEST YOURSELF: Attempt Questions 22.5 and W22.5.

Study SEC exam question 22.2 and model answer in online resources.

DIGITAL CONTENT: A video of this hydrogen-powered car is available on FolensHive.

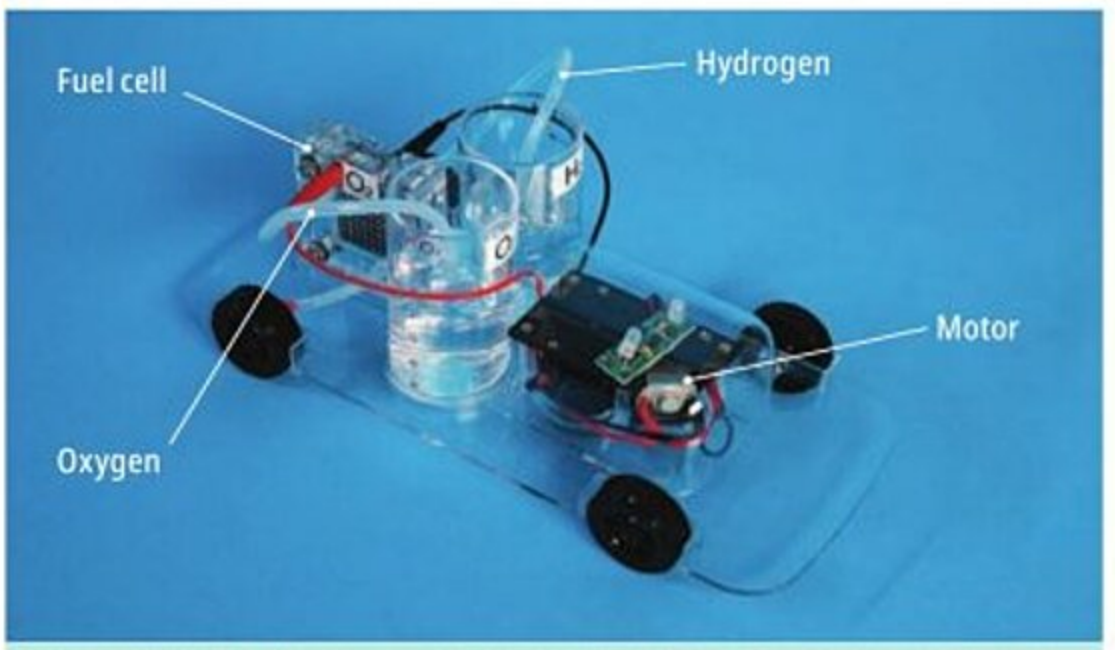


Figure 22.22 This toy car is powered by a hydrogen fuel cell.

22.6 Electrolytic cells

When discussing the recharging of lithium-ion cells we saw that the electric current from the charger could bring about chemical reactions. In other words, the lithium-ion cell was acting as an electrolytic cell.

An **electrolytic cell** is a system in which electricity is used to cause a chemical change that would not happen on its own.

- Therefore, when a lithium-ion cell is discharging, it is acting as a galvanic cell.
- When a lithium-ion cell is being recharged, it is acting as an electrolytic cell.
- A lot of our knowledge about electrolytic cells comes from the work of Michael Faraday, Figure 22.24.

Figure 22.24

Michael Faraday
(1791–1867)

Michael Faraday was one of the greatest science teachers who ever lived. He was a lecturer in chemistry at the Royal Institution in London. His lectures in which he demonstrated lots of experiments drew such large crowds that Albemarle Street where the Royal Institution is located became the first one-way street in London.

- Michael Faraday introduced the word 'electrolysis' into the language of chemistry.
- The word 'electrolysis' comes from two Greek words *electro* and *lysis* which roughly translated mean 'splitting up using electricity'.

Electrolysis is the use of electricity to bring about a chemical reaction in an electrolyte, i.e. a chemical reaction is produced when an electric current is passed through an electrolyte.

NOTE

During electrolysis, the electrode where reduction occurs is still called the cathode and the electrode where oxidation occurs is still called the anode. In other words, CROA applies to both galvanic cells and electrolytic cells.

We can define an electrolyte as follows:

An **electrolyte** is a compound which when molten or dissolved in water will conduct an electric current.

The term *electrolyte* is also used to describe the solution through which a current passes by means of the movement of ions.

An electrolyte can be a conducting liquid or gel.

When carrying out electrolysis experiments, the electrodes we use are usually made of carbon or platinum. This is because these are unreactive and do not react with the electrolyte, Figure 22.25.

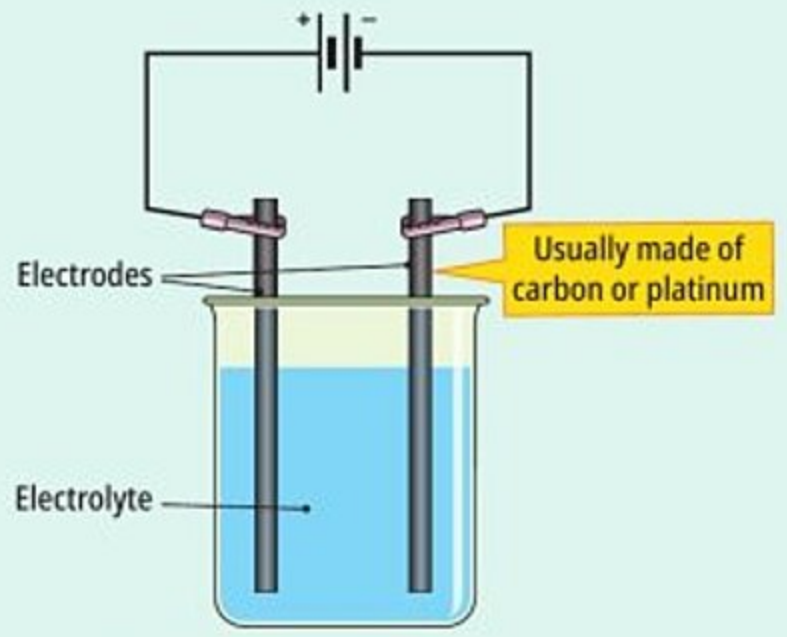


Figure 22.25 When carrying out electrolysis experiments, we use electrodes made of carbon or platinum. This is because these are unreactive and do not react with the electrolyte.

- In most cases, the electrodes do not react with the electrolyte into which they are dipping, i.e. the electrodes merely carry the current in and out of the electrolyte.
- Such electrodes are called **inert electrodes**.
- As mentioned above, the most common inert electrodes are graphite (carbon) and platinum.

We now study three examples of electrolysis reactions.

22.2A Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 22 in the Student Laboratory Notebook.

Student Experiment No. 22

To investigate the electrolysis of acidified water using inert electrodes

Introduction

The main points about this experiment may be summarised as follows:

- An electric current is passed through water to which has been added some dilute sulfuric acid. The sulfuric acid is added to assist the water to conduct electricity.
- The electrolysis reaction is carried out in a Hofmann voltameter or in the type of voltameter that uses inverted test-tubes to collect gases, Figure 22.26.
- A **voltameter** is an apparatus used to study the conduction of electricity through an electrolyte. Do not confuse this name with the name **voltmeter**, which is an instrument used to measure voltage.
- The volume of gas collected at the negative electrode is twice that collected at the positive electrode.
- Samples of each of the two gases are collected and tests are performed on them well away from the apparatus. It is found that the gas at the positive electrode relights a glowing splint, i.e. it is oxygen. The gas formed at the negative electrode ignites with a 'pop', i.e. it is hydrogen.

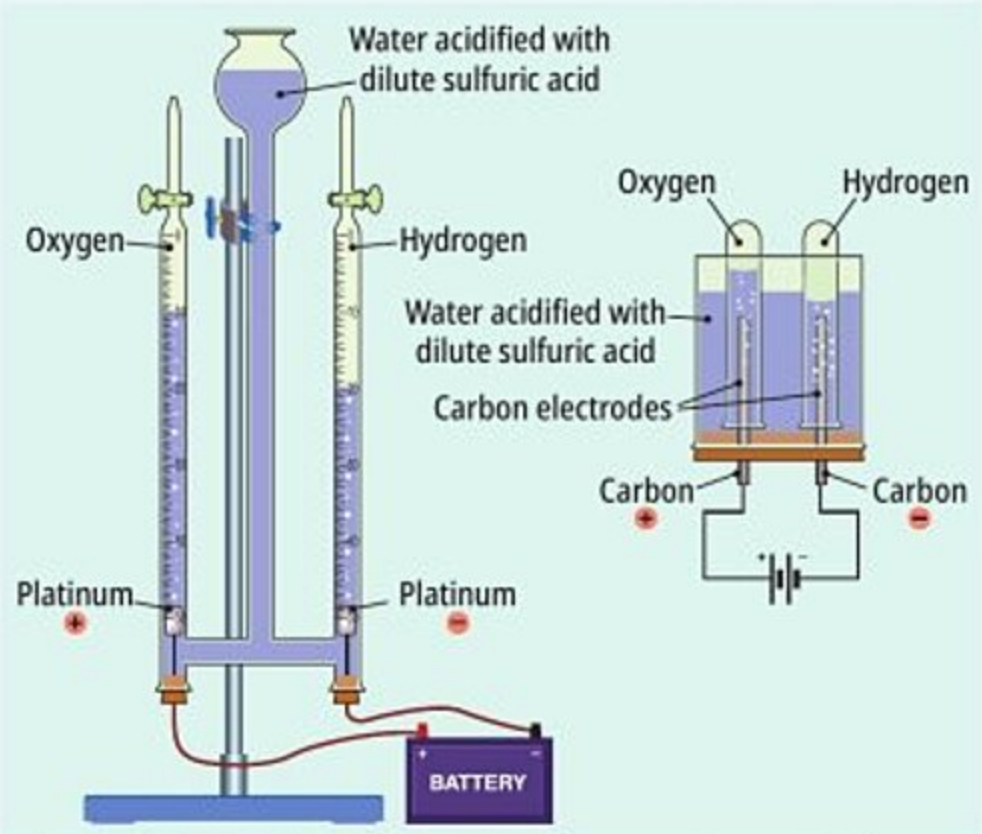


Figure 22.26 Electrolysis of water may be carried out in a Hofmann voltameter or using inverted test-tubes.

- The ratio of hydrogen gas to oxygen gas is 2 : 1 as consistent with the formula H_2O.

The reaction that occurs at the electrode connected to the negative end of the battery is:

Negative electrode: $2H^+ + 2e^- \rightarrow H_2$

The H^+ ions from the sulfuric acid are attracted to the negative electrode. At the negative electrode, each H^+ ion accepts an electron to form a H atom (**reduction**). Two hydrogen atoms then combine to form a hydrogen molecule.

The reaction which occurs at the electrode conned to the positive end of the battery is:

Positive electrode: $H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$

This may also be written as: $H_2O - 2e^- \rightarrow 2H^+ + \frac{1}{2} O_2$

The next few paragraphs are very important. We suggest you have a cup of strong coffee or a large bar of chocolate before you start reading!

You will recall when discussing galvanic cells that the electrode at which oxidation occurs is called the **anode**. Also, the electrode at which reduction occurs is called the **cathode**. We used the acronym CROA to help you remember this. We also learned that in a galvanic cell, the anode was the negative electrode and the cathode was the positive electrode. However, in electrolysis, you will see from the explanations that follow that the cathode is the negative electrode and the anode is the positive electrode.

Let's now take a close look at the reactions that occur in the electrolysis of water.

H^+ ions are attracted to the electrode that is connected to the negative end of the battery and the following reduction reaction occurs:

Negative electrode (reduction): $2H^+ + 2e^- \rightarrow H_2$

Electrons are removed from the water molecules that are near the electrode connected to the positive end of the battery (**oxidation**).

Positive electrode (oxidation): $H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$

This destabilises the water molecule and causes it to break down as shown above. Thus, oxygen gas is evolved at the positive electrode.

Using the acronym CROA, the electrode at which reduction occurs is called the **cathode**. In the electrolysis of water, reduction occurs at the negative electrode. Therefore, in electrolysis, the cathode is the negative electrode. This is the opposite of the situation in galvanic cells where the cathode was the positive electrode.

Using the acronym CROA, the electrode at which oxidation occurs is called the **anode**. In the electrolysis of water, oxidation occurs at the positive electrode. Therefore, in electrolysis the anode is the positive electrode. This is the opposite of the situation in galvanic cells where the anode was the negative electrode.

The reason why the signs are reversed in electrolysis is because the flow of electrons is reversed. In galvanic cells, the flow of electrons resulted from spontaneous chemical reactions. In other words, the reactions happened naturally on their own. However, in electrolysis, we have to force the reactions to occur by applying a voltage to reverse the flow of electrons compared to a galvanic cell.

Negative electrode (reduction):	$2H^+ + 2e^- \rightarrow H_2$
Positive electrode (oxidation):	$H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$
Overall reaction:	$H_2O \rightarrow H_2 + \frac{1}{2} O_2$

Conclusion: Water has been split into hydrogen and oxygen by electrolysis.

Two H^+ ions are removed at the negative electrode and two H^+ ions are produced at the positive electrode. Therefore, the amount of sulfuric acid in the voltameter remains constant and the overall result is that water is broken down into hydrogen gas and oxygen gas.

Note: You may wonder why the SO_4^{2-} ions from the sulfuric acid do not lose their two negative charges by a chemical reaction at the positive electrode. This does not happen because the SO_4^{2-} ions are very stable and cannot be forced to react at this low voltage. If we had used hydrochloric acid, the Cl^- ions in solution would lose their electrons at the positive electrode. This would interfere with the electrolysis of water and would cause chlorine gas to be evolved at the positive electrode instead of oxygen.

- What is essentially happening in any electrolysis reaction is that chemical reactions are occurring at each electrode. The battery 'pumps' electrons on to the negative electrode where they are **gained** by some species, i.e. a **reduction** reaction occurs at the negative electrode.
- At the positive electrode, a chemical reaction occurs that involves a **loss** of electrons, i.e. an **oxidation** reaction occurs.

22.2B Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 22 in the Student Laboratory Notebook.

Student Experiment No. 22

To investigate the electrolysis of copper(II) chloride solution using inert electrodes

Introduction

The main points about this experiment may be summarised as follows:

- Some copper(II) chloride solution is poured into a beaker.
- Two carbon electrodes are placed into the solution and connected to the DC power supply, Figure 22.27.

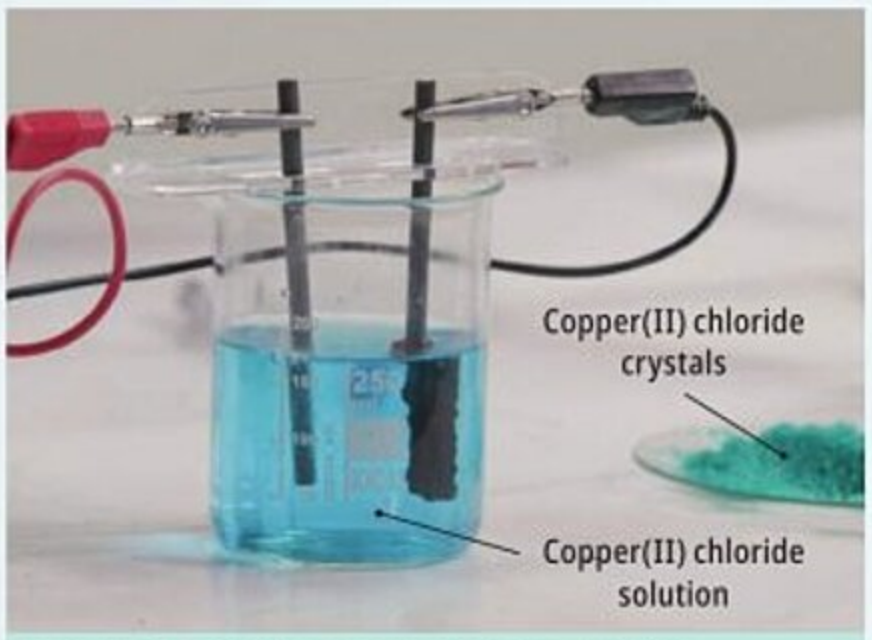


Figure 22.27 Electrolysis of copper(II) chloride solution

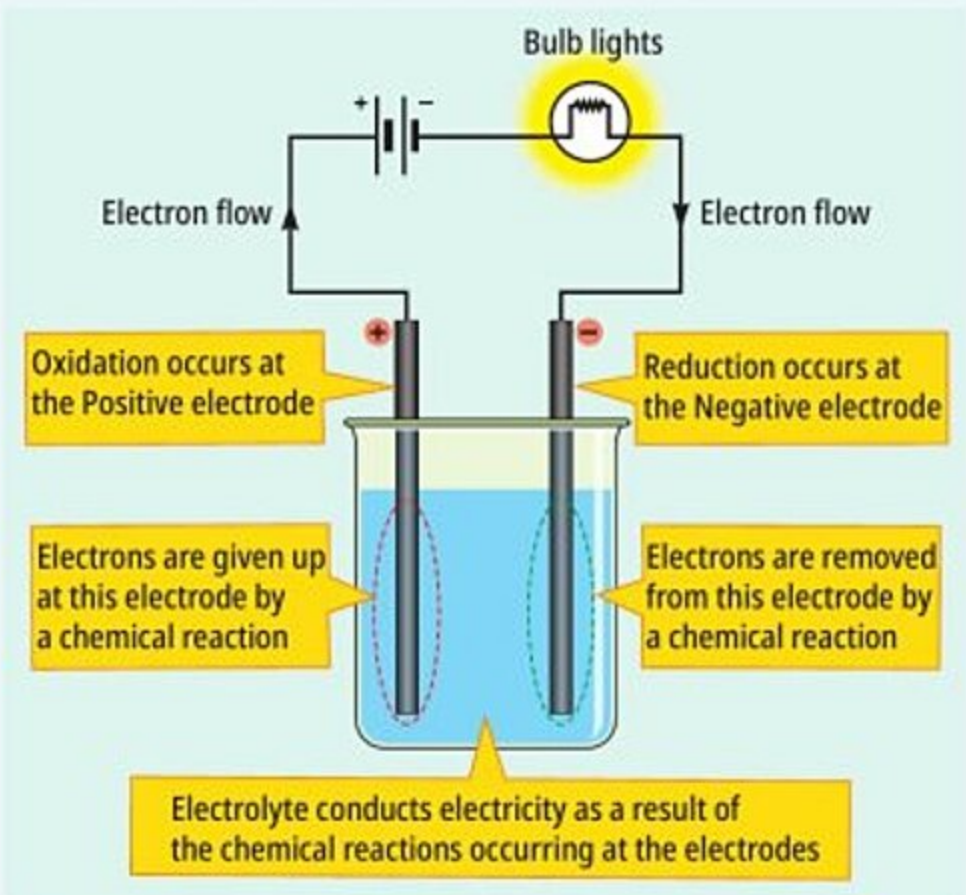

Bulb lights
Electron flow
Electron flow
Oxidation occurs at the Positive electrode
Reduction occurs at the Negative electrode
Electrons are given up at this electrode by a chemical reaction
Electrons are removed from this electrode by a chemical reaction
Electrolyte conducts electricity as a result of the chemical reactions occurring at the electrodes

Figure 22.27a Since electrons are being removed from one electrode and given up at the other electrode, there is a complete circuit.

- The power supply is switched on and observations noted.
- It is observed that a brown solid is formed at the electrode connected to the negative end of the power supply.
- This solid is copper metal.

Negative electrode (reduction at cathode): $Cu^{2+} + 2e^- \rightarrow Cu$

- It is observed that bubbles of gas are collected at the electrode connected to the positive end of the power supply.
- If the gas is tested with moist blue litmus paper, it is observed that the litmus paper is bleached. This suggests that the gas is chlorine.

Positive electrode (oxidation at anode): $2Cl^- \rightarrow Cl_2 + 2e^-$

Overall reaction: $Cu^{2+} + 2Cl^- \rightarrow Cu + Cl_2$

Conclusion

During electrolysis of copper(II) chloride solution, copper metal is deposited at the cathode and chlorine gas is released at the anode. Note that since electrons are being removed from one electrode and given up at the other electrode, there is a complete circuit, Figure 22.27a.

22.2C Experiment

Full details of the procedure for carrying out this experiment are given in Experiment 22 in the Student Laboratory Notebook.

Student Experiment No. 22

To investigate what happens when an electric current is passed through a solution of potassium iodide using inert electrodes

Introduction

In this electrolysis experiment, a gas is given off at only **one** electrode. The experiment may be carried out conveniently in the apparatus shown in Figure 22.28. The iodine that is formed is more easily seen if platinum electrodes are used.

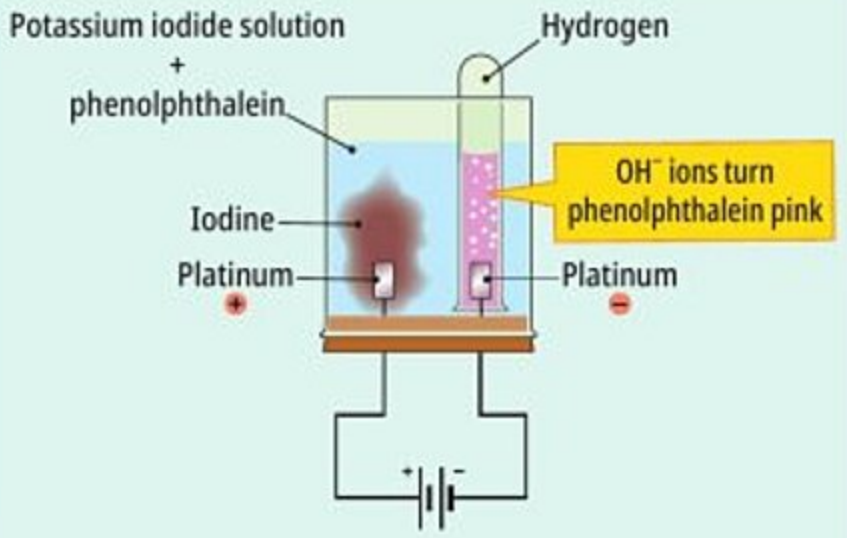


Figure 22.28 Iodine and hydrogen gas are formed when a solution of potassium iodide is electrolysed.

The main points about this experiment may be summarised as follows:

- Some potassium iodide solution is placed in the apparatus shown and a few drops of phenolphthalein indicator are added. The solution is colourless.
- As the electrolysis proceeds, a brown colour is observed at the positive electrode, Figure 22.29.
- The brown colour at the positive electrode is due to the formation of iodine. The negative iodide ions in the water are attracted to the positive electrode ('unlike charges attract'). At the positive electrode, each iodide ion loses an electron to form an iodine atom. Two iodine atoms then join together to form an iodine molecule.

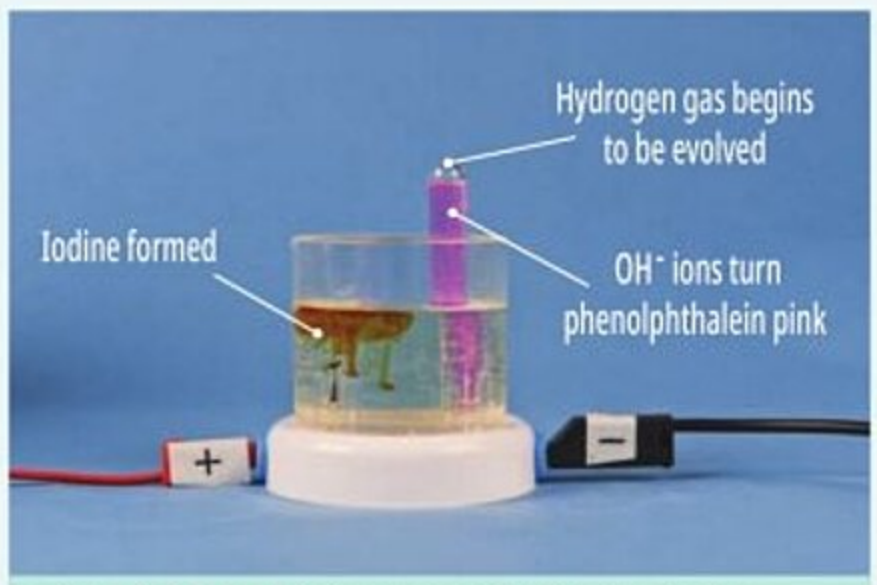


Figure 22.29 Electrolysis of KI solution is taking place in this voltameter.

Positive electrode (oxidation at anode):

$$2I^- \rightarrow I_2 + 2e^-$$

Oxidation is occurring at the positive electrode since electrons are being lost.

- A pink colour is observed at the negative electrode and a gas is evolved. The gas is collected in a test-tube and is found, on analysis, to be hydrogen. The fact that the phenolphthalein turns pink implies that the solution is turning alkaline (OH^- ions present). Phenolphthalein is pink in a base and colourless in an acid. These facts lead chemists to conclude that the following reaction occurs at the negative electrode:

Negative electrode (reduction at cathode): $2H_2O + 2e^- \rightarrow H_2 + 2OH^-$

Reduction occurs at the negative electrode as electrons are being gained.

Overall reaction: $2I^- + 2H_2O \rightarrow I_2 + H_2 + 2OH^-$

Conclusion

When a solution of potassium iodide undergoes electrolysis, the products are iodine, hydrogen gas and hydroxide ions.

Thus, what is actually happening at the negative electrode is that water molecules are being forced to accept electrons from the negative electrode. These extra electrons cause the molecules to be destabilised, and they break up to form hydrogen gas and hydroxide ions.

22.7 Concluding points

We began our study of electrochemistry by discussing galvanic (voltaic) cells and completed our study by discussing electrolytic cells. Both types of cells may be classified under the general category of electrochemical cell.

An **electrochemical cell** is any system that converts chemical energy into electrical energy or electrical energy into chemical energy by means of a redox reaction.

In other words, an electrochemical cell is a device that either (i) uses chemical reactions to produce electricity or (ii) uses electricity to cause chemical reactions to take place. In both cases, electrons move from one substance to another, i.e. oxidation-reduction reactions occur.

The final learning outcome that needs to be covered in this chapter is the following learning outcome specified in the syllabus:

- **Students should be able to research a role of electrochemistry in an area related to sustainability and technology in everyday life.**

In specifying the depth of treatment associated with this learning outcome the following two points are given:

- How electrochemistry could provide more sustainable uses of energy, such as electrochemical cells and the use of rechargeable batteries.
- Electrolysis and its potential for hydrogen production as a fuel, for example, through electricity generated from sustainable sources.

Your teacher may provide this research investigation as homework for you. When carrying out your research the following guidelines may be of assistance:

- Begin with a clear focus and choose **one** main area to research, such as:
  - Electrochemical cells and rechargeable batteries (e.g. lithium-ion batteries in electric vehicles).
  - Electrolysis for hydrogen fuel production (especially using renewable electricity).
- Make sure that you understand the basic scientific concepts explained in this chapter:
  - Key terms such as *redox reactions*, *anode*, *cathode*, *galvanic cells* and *electrolytic cells*.
  - Be able to explain how redox reactions and ion flow are involved in galvanic cells and electrolytic cells.
- Make the link to sustainability:
  - Explain how the technology reduces the dependence on fossil fuels.
  - Examine the environmental impact of materials used (e.g. materials in batteries).
  - Compare and contrast the use of items such as petrol cars versus electric cars.
- Include real-world examples:
  - Research how these new technologies (e.g. electric battery technology and hydrogen for transport) are being brought into use in other countries.
  - Compare what is happening in other countries with what is happening in Ireland.
- Use reliable sources:
  - Scientific websites (websites from reputable government organisations and professional bodies).
  - Reputable news articles on green technology innovations.
  - Avoid blogs or commercial sites.
- Analyse the material that you have gathered:
  - What are the advantages and limitations of the technology?
  - Are there economic or practical challenges in large-scale use?
- Summarise your conclusions and recommendations (e.g. in a PowerPoint presentation):
  - Use diagrams of galvanic or electrolytic cells.
  - Define all scientific terms used.
  - Connect your research to everyday applications or current events.

TEST YOURSELF: Attempt Questions 22.6–22.7 and W22.6–W22.10.

Summary What I should know

- A galvanic (voltaic) cell is a device that converts chemical energy into electrical energy through oxidation-reduction reactions that occur within it.
- The electrochemical series is a list of elements in order of their standard electrode potentials, i.e. in order of the decreasing tendency for the element to be oxidised (lose electrons) under standard conditions.
- A metal will displace another metal that is below it in the electrochemical series from a solution of its ions.
- A primary cell is a type of galvanic cell that cannot be recharged.
- A secondary cell is a type of galvanic cell that can be recharged.
- A fuel cell is a device that converts the chemical energy stored in a fuel fed into the fuel cell directly into electrical energy.
- Electrolysis is the use of electricity to bring about a chemical reaction in an electrolyte.
- An electrolytic cell is a system in which electricity is used to cause a chemical change that would not happen on its own.
- The electrode at which reduction occurs is called the cathode and the electrode where oxidation occurs is called the anode (CROA).
- In a galvanic cell, the cathode is the positive electrode, and the anode is the negative electrode. However, in an electrolytic cell, the cathode is the negative electrode, and the anode is the positive electrode.
- An electrochemical cell is any system that converts chemical energy into electrical energy or electrical energy into chemical energy by means of redox reactions.

Learning outcomes

At the end of this chapter, I should be able to:			
Describe and explain the operation of a galvanic cell.			
Investigate displacement reactions of metals and relate them to the electrochemical series.			
Define a primary and secondary cell and compare them.			
Explain the operation of a simple hydrogen fuel cell and compare a chemical cell with a fuel cell.			
Discuss the electrolysis of acidified water, copper(II) chloride solution and potassium iodide solution using inert electrodes.			
Research a role of electrochemistry in an area related to sustainability and technology in everyday life.			

Chapter review questions

22.1 **(a)** What did Luigi Galvani observe during his experiment with a frog's leg?

(b) In what way did Galvani misinterpret the findings of his experiment?

(c) What was Alessandro Volta's explanation for Galvani's findings?

(d) What did Volta build in 1800 to produce electricity?

(e) What is meant by the term *electrochemistry*?

(f) What are the two main branches of electrochemistry?

22.2 **(a)** What is the approximate voltage generated by the zinc–copper cell?

(b) Explain why the voltage of a single half-cell cannot be measured directly.

(c) What is the electrochemical series?

(d) Describe how the electrochemical series can be used to predict chemical reactions.

(e) Why does magnesium displace copper in solution?

(f) What reaction occurs when copper metal is placed in a solution of silver nitrate?

22.3 The following are some metals in order of decreasing ease of oxidation as they appear in the electrochemical series:

- Sodium
- Magnesium
- Zinc
- Iron
- Copper

Answer the following questions with reference to these metals.

(a) Which one of the five metals corrodes most easily?

(b) What method is used, in the school laboratory, to protect this metal from corrosion?

[LCH]

22.4 **(a)** What is the difference between a cell and a battery?

(b) Explain why zinc-carbon cells and alkaline cells are called primary cells.

(c) What is the approximate voltage of a lithium-ion cell?

(d) Why are lithium-ion cells classified as secondary cells?

(e) Why is only one lithium-ion cell needed in a smartphone? Give one advantage of using just a single cell in a smartphone.

(f) Explain why lithium-ion batteries have the potential to reduce the environmental impact of transport.

22.5 **(a)** Explain why a fuel cell is considered a type of galvanic cell.

(b) What type of energy transformation occurs in a fuel cell?

(c) What fuel and oxidising agent are used in a hydrogen fuel cell?

(d) What is the function of the porous carbon and platinum catalyst at the anode of a hydrogen fuel cell?

22.6 **(a)** Explain the difference between a galvanic cell and an electrolytic cell.

(b) What word did Michael Faraday introduce into the language of electrochemistry?

(c) Why are carbon and platinum electrodes commonly used in many electrolysis experiments?

(d) Why is sulfuric acid added to water in the electrolysis of water experiment?

(e) Write the oxidation half-equation at the positive electrode during electrolysis of acidified water.

(f) Discuss the reversal of electrode signs between galvanic and electrolytic cells.

22.7 **(a)** Explain the meaning of the terms *electrolysis*, *electrolyte*, *electrode*.

(b) A solution of potassium iodide to which a few drops of phenolphthalein indicator have been added is electrolysed using inert electrodes.

(i) Name a suitable material for use as electrodes.

(ii) Describe what you observe as the electrolysis proceeds.

(iii) Write ionic equations to describe the reactions happening at the electrodes.

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	I	II									III	IV	V	VI	VII	VIII
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
n = 1																		2 HELIUM He 4.003
n = 2	3 LITHIUM Li 6.941	4 BERYLLIUM Be 9.012											5 BORON B 10.81	6 CARBON C 12.01	7 NITROGEN N 14.01	8 OXYGEN O 16.00	9 FLUORINE F 19.00	10 NEON Ne 20.18
n = 3	11 SODIUM Na 22.99	12 MAGNESIUM Mg 24.31											13 ALUMINIUM Al 26.98	14 SILICON Si 28.09	15 PHOSPHORUS P 30.97	16 SULFUR S 32.07	17 CHLORINE Cl 35.45	18 ARGON Ar 39.95
n = 4	19 POTASSIUM K 39.10	20 CALCIUM Ca 40.08	21 SCANDIUM Sc 44.96	22 TITANIUM Ti 47.87	23 VANADIUM V 50.94	24 CHROMIUM Cr 52.00	25 MANGANESE Mn 54.94	26 IRON Fe 55.85	27 COBALT Co 58.93	28 NICKEL Ni 58.69	29 COPPER Cu 63.55	30 ZINC Zn 65.41	31 GALLIUM Ga 69.72	32 GERMANIUM Ge 72.64	33 ARSENIC As 74.92	34 SELENIUM Se 78.96	35 BROMINE Br 79.90	36 KRYPTON Kr 83.80
n = 5	37 RUBIDIUM Rb 85.47	38 STRONTIUM Sr 87.62	39 YTTRIUM Y 88.91	40 ZIRCONIUM Zr 91.22	41 NIOBIUM Nb 92.91	42 MOLYBDENUM Mo 95.94	43 TECHNETIUM Tc (97.91)	44 RUTHENIUM Ru 101.1	45 RHODIUM Rh 102.9	46 PALLADIUM Pd 106.4	47 SILVER Ag 107.9	48 CADMIUM Cd 112.4	49 INDIUM In 114.8	50 TIN Sn 118.7	51 ANTIMONY Sb 121.8	52 TELLURIUM Te 127.6	53 IODINE I 126.9	54 XENON Xe 131.3
n = 6	55 CAESIUM Cs 132.9	56 BARIUM Ba 137.3	57 LANTHANUM La 138.9	72 HAFNIUM Hf 178.5	73 TANTALUM Ta 180.9	74 TUNGSTEN W 183.8	75 RHENIUM Re 186.2	76 OSMIUM Os 190.2	77 IRIDIUM Ir 192.2	78 PLATINUM Pt 195.1	79 GOLD Au 197.0	80 MERCURY Hg 200.6	81 THALLIUM Tl 204.4	82 LEAD Pb 207.2	83 BISMUTH Bi 208.98	84 POLONIUM Po (209.0)	85 ASTATINE At (210.0)	86 RADON Rn (222.0)
n = 7	87 FRANCIUM Fr (223.0)	88 RADIUM Ra (226.0)	89 ACTINIUM Ac (227.0)	104 RUTHERFORDIUM Rf (261.1)	105 DUBNIUM Db (262.1)	106 SEABORGIUM Sg (266.1)	107 BOHRIUM Bh (264.1)	108 HASSIUM Hs (277.0)	109 MEITNERIUM Mt (268.1)	110 DARMSTADTIUM Ds (271)	111 ROENTGENIUM Rg (272.2)	112 COPERNICIUM Cn (285)	113 NIHONIUM Nh (286)	114 FLEROVIUM Fl (289)	115 MOSCOVIUM Mc (289)	116 LIVERMORIUM Lv (293)	117 TENNESSINE Ts (294)	118 OGANESSON Og (294)

1 HYDROGEN H 1.008 — 1 Atomic number; Name; Symbol; Relative atomic mass

f-block

● Lanthanoid series	58 CERIUM Ce 140.1	59 PRASEODYMIUM Pr 140.9	60 NEODYMIUM Nd 144.2	61 PROMETHIUM Pm (144.9)	62 SAMARIUM Sm 150.4	63 EUROPIUM Eu 152.0	64 GADOLINIUM Gd 157.3	65 TERBIUM Tb 158.9	66 DYSPROSIUM Dy 162.5	67 HOLMIUM Ho 164.9	68 ERBIUM Er 167.3	69 THULIUM Tm 168.9	70 YTTERBIUM Yb 173.0	71 LUTETIUM Lu 175.0
● Actinoid series	90 THORIUM Th 232.0	91 PROTACTINIUM Pa 231.0	92 URANIUM U 238.0	93 NEPTUNIUM Np (237.0)	94 PLUTONIUM Pu (244.1)	95 AMERICIUM Am (243.1)	96 CURIUM Cm (247.1)	97 BERKELIUM Bk (247.1)	98 CALIFORNIUM Cf (251.1)	99 EINSTEINIUM Es (252.1)	100 FERMIUM Fm (257.1)	101 MENDELEVIUM Md (258.1)	102 NOBELIUM No (259.1)	103 LAWRENCIUM Lr (262.1)

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- **Accessible content:** Clear, student-friendly language with engaging diagrams, graphs, tables, and illustrations
- **Curriculum clarity:** Teaching objectives and learning outcomes clearly signposted
- **Higher Level signposting:** Higher Level content highlighted for easy reference
- **Experiment support:** Key points of all student experiments specified in the new curriculum are included. Full, step-by-step procedures feature in the Student Laboratory Notebook and online videos.
- **Worked examples:** Step-by-step worked examples that reinforce key concepts
- **Exam focus:** Sample exam questions and model answers based on SEC sample papers
- **Built-in revision:** Practice and revision built into every chapter.

Also available in the teaching package:

- eBook
- Assessment and Exam Guide
- Student Laboratory Notebook
- Teacher's Guide
- Online teaching resources
- Experiment videos for students

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